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**PROCEEDINGS
of the
TENTH COTTON UTILIZATION RESEARCH CONFERENCE**

**Held at
New Orleans, Louisiana
April 29 to May 1, 1970**

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**Agricultural Research Service
UNITED STATES DEPARTMENT OF AGRICULTURE**

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CONTENTS

	Page
Welcome	
C. H. Fisher	1
Opening Remarks	
L. Aubrey Goodson, Jr.	2
Systems Analysis of Cotton Research	
Steven C. King	3
FIRST SESSION: Ludwig Rebenfeld, Chairman	
Comparison of Structures and Properties of Cotton Crosslinked by Pad-Dry-Cure, Mild Cure, Poly-Set, and Wet-Fix Processes. I. Physical Properties of Fibers, Yarns, and Fabrics	
James N. Grant, Frederick R. Andrews, and Louis C. Weiss (Presented by James N. Grant)	7
Comparison of Structures and Properties of Cotton Crosslinked by the Pad-Dry-Cure, Mild Cure, Poly-Set, and Wet-Fix Processes. II. Swelling Behaviors in Caustic Solution	
Edith Honold and James N. Grant (Presented by Edith Honold)	9
Comparison of Structures and Properties of Cotton Crosslinked by Pad-Dry-Cure, Mild Cure, Poly-Set, and Wet-Fix Processes. III. Structural Considerations of the Crosslinked Celluloses	
S. P. Rowland, S. M. Stark, Jr., V. O. Cirino, and J. S. Mason (Presented by S. P. Rowland)	11
Effect of Temperature on the Infrared Absorption of Celluloses	
E. R. McCall, N. M. Morris, V. W. Tripp, and R. T. O'Connor (Presented by E. R. McCall)	14
SECOND SESSION: Richard D. Gilbert, Chairman	
Investigation on the Chemical Structure of Crosslinked Cotton	
K. Heinisch, A. Katayama, H. K. Rouette, Angelika Wehner, and H. Zollinger (Presented by H. Zollinger)	17
Influence of the Catalyst in Cotton-Epoxy Reactions	
J. B. McKelvey, R. J. Berni, and R. R. Benerito (Presented by J. B. McKelvey)	25
The Effect of Light on Cotton in the Absence and Presence of Anthraquinonoid Dyes	
Glyn O. Phillips	27
High-Strength Cotton Knit Fabric with Durable-Press Performance and High Laundering Life, Prepared from Mercerized Yarn	
Alton L. Murphy, Matthew F. Margavio, and Clark M. Welch (Presented by Alton L. Murphy)	30
Hydrophilicity in Fluorochemical Stain Release Polymers	
A. G. Pittman, J. N. Roitman, and D. L. Sharp (Presented by J. C. Arthur, Jr.)	32
THIRD SESSION: John Compton, Chairman	
Chemical-Mechanical Combination Treatments for Durable-Press Cottons	
Glenn P. Morton, David M. Hall, and J. David Reid (Presented by Glenn P. Morton)	34
The Effect of Formaldehyde Crosslinking of Cotton on the Chain Length of the Cellulose Molecule. I. The Form W' Process	
Leon Segal and J. D. Timpa (Presented by Leon Segal)	36
Methods for Reduction of Free Formaldehyde in Carbamate-Sensitized Fabrics	
J. David Reid, Russell M. H. Kullman, and Robert M. Reinhardt (Presented by J. David Reid)	38
Decrystallization of Cotton Cellulose Yarns by Dual-Treatments with Quaternary Ammonium Hydroxides and Alkali Metal Hydroxides	
Tyrone L. Vigo, Donald Mitcham, and Clark M. Welch (Presented by Tyrone L. Vigo)	40
Mineral Dyeing Process for Cotton to Impart Mildew and Weather Resistance	
Hubert H. St. Mard, Carl Hamalainen, and Albert S. Cooper, Jr. (Presented by Hubert H. St. Mard)	42

CONTENTS (Continued)

	Page
FOURTH SESSION: James S. Parker, Chairman	
Utilization of Discount Cotton in Yarn Manufacturing Jack D. Towery, Robert L. Mouchet, and Harry E. Arthur (Presented by Harry E. Arthur)	44
The Durable Press Performance of Fabrics Prepared from Blends of Cotton and Resin Sensitized Cotton G. A. M. Butterworth, Laurance G. Coffin, Milton M. Platt, and Emery C. Kingsbery (Presented by G. A. M. Butterworth)	46
Durable Press Denims Woven from Polymer Sized Yarns John T. Lofton, Robert J. Harper, C. O. Graham, and Eugene J. Blanchard (Presented by C. O. Graham) .	49
Light Scattering Studies on Cotton to Aid Instrument Design George J. Doyle	50
Fibers, Fields and Forces Albert Baril, Jr. and James M. Hemstreet (Presented by Albert Baril, Jr.)	68
FIFTH SESSION: Harry M. Keeton, Chairman	
The Effects of Weathering on the Laundering Durability of Fire-Resistant Cotton Fabrics David A. Yeadon, Gary F. Danna, Albert S. Cooper, Jr., and Wilson A. Reeves (Presented by David A. Yeadon)	70
Photochemical and Thermal Degradation of Selected Flame Retardants L. W. Mazzeno, Jr., H. M. Robinson, E. R. McCall, and N. M. Morris (Presented by L. W. Mazzeno, Jr.)	72
Protection of Flame Retardants from Actinic Degradation Ralph J. Brysson, Albert M. Walker, and Albert S. Cooper, Jr. (Presented by Ralph J. Brysson)	74
Methylol Derivative of Tris(2-carbamoyl-ethyl)phosphine Oxide as a Flame Retardant for Cotton Cletus E. Morris, Leon H. Chance, George L. Drake, Jr., and Wilson A. Reeves (Presented by Cletus E. Morris)	76
Effects of Mole Fraction of "THPOH" in THPC—"THPOH" Formulations and Cure Conditions on Flame-Retardant Fabrics John V. Beninate, George L. Drake, Jr., and Wilson A. Reeves (Presented by John V. Beninate)	77
Attendance list	78

WELCOME

by

C. H. Fisher

Director

Southern Utilization Research and Development Division

New Orleans, La.

To the members of Tenth Cotton Utilization Research Conference: Good morning, greetings, and welcome. We in the Southern Utilization Research and Development Division (SURDD) of the U. S. Department of Agriculture appreciate your interest in cotton and in our cotton research.

These conferences have been successful in the past, and I'm certain that this conference also will be successful. We have all the elements needed for a successful conference: splendid audience, excellent program and speakers, distinguished leaders in textile research to serve as chairmen, and a distinguished member of USDA to give the keynote address.

I think you must know the principal purpose of these annual cotton research conferences. The principal purpose is to provide us in SURDD the privilege of reporting promptly on advances in our cotton research during the past year and to give you the opportunity of hearing about our recent research and commenting on it.

We want and appreciate your interest. We invite you to comment, present questions, and even to criticize if you wish to do so. We also invite you to visit us and to communicate with us during the year, on any occasion.

These annual conferences are not our only means of disseminating information about our research. We publish the results of our research — approximately 150 publications per year. Our scientists and engineers present talks at technical meetings. USDA's Extension Service and the Information Division of ARS provide valuable assistance. L. L. Heffner, at Raleigh, N. C., and Wm. Martin at Clemson, are two members of the Extension Service who perform an excellent service by reporting on advances in cotton research. Our ARS Information Division, headquartered in Washington, helps in telling the

cotton story, too. The local representative, V. R. Bourdette, arranged a style show for our conference. You will hear more about this later.

We have just passed through the decade of the 60's — and we are entering the decade of the 70's. This is our Tenth Annual Cotton Utilization Conference.

I shall resist the temptation to review the past — and to project the future. I do wish, however, to thank our friends in many organizations for their interest and help during the 60's and for support of our conferences. We in this Division don't work alone. We have a cooperative program. We appreciate the privilege of working with many individuals and organizations.

I also thank my colleagues in the Division for their competent and dedicated research. This research has brought many advances in cotton science and technology; has contributed to a number of developments used commercially; has benefitted cotton materially in its competition with other fibers; and brought honors and special recognition to our individual scientists and engineers.

Many have made predictions about textiles in the 70's. I'll mention the most recent one to come to my attention — one published in the April 20, 1970, issue of Chemical and Engineering News. This article predicts a great future for textiles in general. A modest increase in cotton consumption is predicted.

I wish to thank everyone contributing to the success of this conference, including B. H. Wojcik and his assistants; General Chairman L. Aubrey Goodson, Jr.; our Session Chairmen; our speakers; and all members of this excellent audience.

OPENING REMARKS

by

L. Aubrey Goodson, Jr.
Vice President and Director of Research
Dan River Mills, Inc.
Danville, Va.

I am honored to be general chairman of the Tenth Cotton Utilization Research Conference. This is one of the most respected and best attended technical programs serving the textile industry in general, and the chemistry of cotton in particular.

I am here as a representative of a weaving organization founded on cotton textiles. We have a heavy investment in cotton spinning, weaving, and finishing equipment. Cotton chemistry is a way of life for us. Dan River Mills has a very real interest in cotton and its future. It is a strong bond of common interest that links us to the efforts of the Southern Utilization Research and Development Division here in New Orleans.

It is the fruit of the efforts of that group — namely basic knowledge that we have the privilege of sharing. I have been increasingly impressed with the depth and substance of this group's understanding of the product they serve. Their findings lay a foundation for all of us to build on. This knowledge is the starting point in enabling cotton to satisfy the consumer needs of the seventies. It is the base for all of the promotional efforts of the cotton industry. It is a keystone in producing a better product and selling it more efficiently and more effectively.

I am pleased that all of us can share that knowledge. I am honored to have a small part in presenting it to you.

SYSTEMS ANALYSIS OF COTTON RESEARCH

by

Steven C. King
Assistant Director
Science and Education Staff, USDA
Washington, D. C.

Cotton is an important crop in domestic and export markets. It represents a critical supply-management problem for the Nation. It is under severe competitive pressure from man-made fibers and from foreign cotton producers. Cotton is no longer "King Cotton," but a commodity beset with problems. However, it is represented by an organized industry, one with the power to develop and maintain a political urgency with respect to the solution of its problems.

PURPOSE OF THE STUDY

The purpose of this study is to conduct an evaluative analysis of the problems faced by the cotton industry and to present the results in a meaningful way to assist policymakers in making decisions about future cotton research programs. The cotton industry has recognized its serious situation and has identified the problems, the solutions of which, it believes represent its salvation. The National Cotton Council of America developed in 1967 a "Master Blueprint for Cotton Research." While the

"Master Blueprint" is a monumental effort, it is based on the assumption that every avenue of research that has potential for improving cotton's position should be pursued. However, the Department and the State Stations need an analysis of the research problems posed by the cotton situation that offers alternatives, the pay-offs for each and considers the likely extenuating consequences of choosing one or more alternatives.

SCOPE OF THE STUDY

Our basic concern is the continuation of the cotton industry as a major agricultural and industrial enterprise in the United States. The scope of this study, then, must encompass the entire industry from production of cotton bolls to problems that concern consumer use of cotton products. Figure 1 presents in a schematic way the breadth of our concern. Each element affects the succeeding element(s) in the diagram and factors within an element may affect not only other factors within the element, but also may have far-reaching implications in preceding elements.

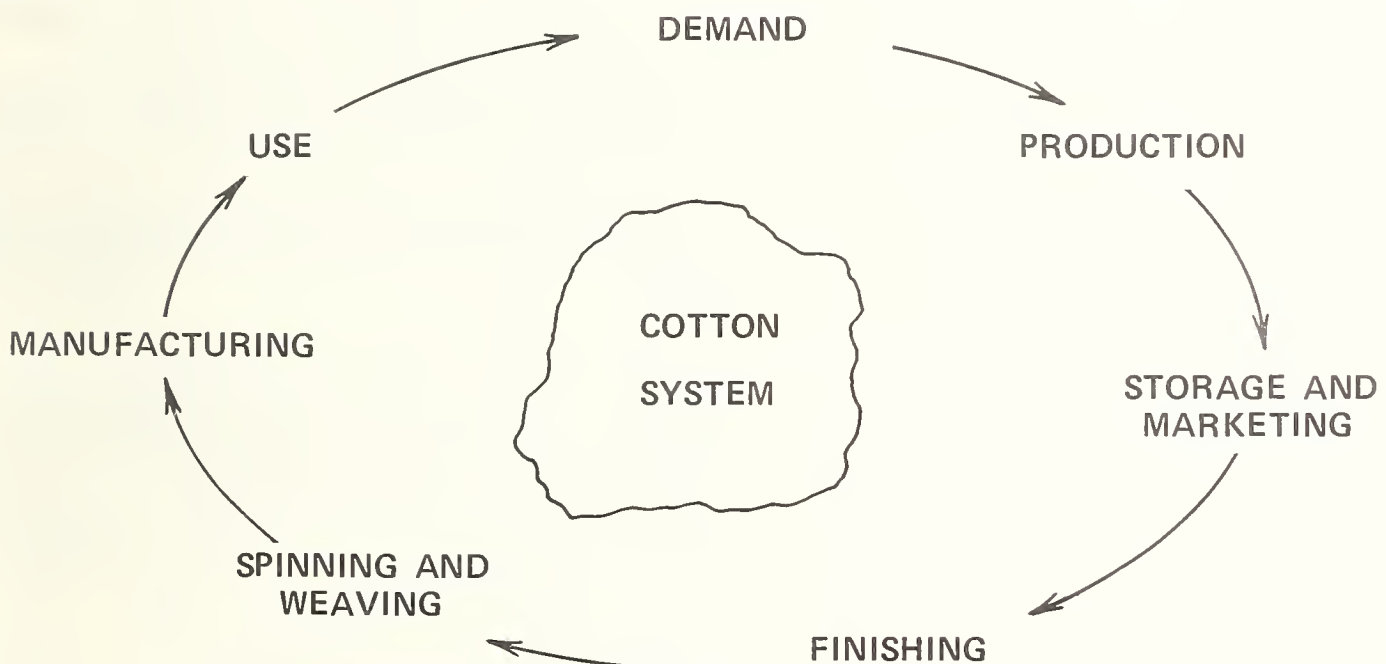


Figure 1.

The interest in this study is in research activities only. That is, what can research do that will lead to the solution of cotton's problems? The answer to this question must include identification of the problems, estimation of the economic and social costs related to each problem, specification of what research can do toward solving the problem, estimation of research and other costs required to reap the benefits of new technology developed, and consideration of the consequences incident to the adoption of that technology.

PROCEDURES

This study was organized as a small ad hoc study group under Research Progress Development and Evaluation Staff's (RPDES) leadership. The members of the study group were as follows:

Steven C. King, RPDES, Chairman
Horace L. Puterbaugh, Agricultural Research Service (ARS)
Irving R. Starbird, Economic Research Service (ERS)
Roland R. Robinson, Cooperative State Research Service (CSRS)

From time to time other members of the Department have contributed their efforts to the study by making special analyses or providing technical advice concerning the research problems being evaluated. Field visits to Louisiana, Mississippi, and South Carolina were valuable in giving orientation to the study group and in furnishing technical data and suggestions from Department and State Station scientists and also from industry representatives.

The plan of the study was developed within an environment that recognized a number of broad policy goals of the Department and of industry.

Goals for cotton industry:

1. Improve farm income of cotton producers.
2. Maintain or increase cotton's share of the domestic fiber market.
3. Increase the export market for cotton.
4. Reduce or eliminate the need for cotton control and support programs.

I think you'll immediately recognize that some of these goals are also national goals. However, a cotton industry goal need not necessarily be a national goal, because a cotton industry goal may offset some other goal and thus provide no net national benefit. In fact, achieving one of these cotton industry goals may have impacts that cause us to fall short on another cotton industry goal.

For example, if we reduce the cost of producing cotton and a large increase in yield is one of the consequences, what are we to do with the excess acres? Won't we need to find other alternatives for many cotton farmers? Won't we be running counter to our goal of reducing or eliminating the need for control and support programs? Unless we can sell more cotton at the reduced price, we'll have less income to divide among the cotton producers.

I call your attention to this particular problem, because it's a familiar one in agriculture. We haven't found a way to lick it yet.

So, these are goals for the cotton industry and goals that the Department of Agriculture can support. However, they are goals that conflict and goals which the Nation as a whole will find conflicting with other national goals.

Beginning with the basic system shown in figure 1, the study group employed the systems approach to analyze each subsystem. This involved developing a work breakdown structure for each subsystem, so that each operation of the subsystem could be analyzed in some depth. The key steps in this analysis were:

Analytical steps:

- Estimate current cost for each operation
- Estimate costs in 1980 given current knowledge
- Estimate the potential reduction in costs
- Estimate 1980 costs given new technology
- Determine net benefit possible by 1980
- Estimate costs of obtaining and applying new technology
- Benefit/cost ratio for each new technology
- Estimate demand for cotton in 1980
- Evaluate consequences of adopting new technologies
- Determine the priority for each research activity

Now, how did we carry out each of the 10 steps in our systems analysis?

1. *Estimate current cost for each operation.* — We used ERS's 1966 cost of production data. If the 1968 data are complete before we finish the study, we'll update.

2. *Estimate costs in 1980 given current knowledge.* — We asked a panel of production research scientists to tell us how much costs would change from 1966, given 1966 dollars. The stipulation was that no new scientific knowledge would be generated, but farmers could make fuller adoption of technology already known. We're not saying to discontinue research. What we needed was a base point to establish costs for new technology that comes on stream after 1966.

3. *Estimate the potential reduction in costs.* — We asked the scientists to predict the total possible changes in costs from application of conceivable new technology without regard to time of completion of research or adoption. This is a hard task. Robert Ayres, in his book "Technical Forecasting and Long-Range Planning," points out repeated incidents where the so-called "experts" missed by a mile in predicting new technology. For the most part the experts were far too conservative. Many couldn't even see developments in their own field of science. Buck Rogers was a better predictor of today's space technology than the authorities of the day.

4. *Estimate 1980 costs given new technology.* — Quite obviously, we don't expect to achieve all the possible benefits from new technology within 10 years' time. So, we stake out that portion that we think we can realize and estimate what it will cost to do each operation given whatever level of adoption we have been able to achieve.

5. *Determine net benefit possible by 1980.* — This is the difference between the last step and the 1980 cost given the 1966 level of knowledge (step 2).

6. *Estimate costs of obtaining and applying new technology.* — We ask the scientists to predict how many scientist man-years of effort will be required to bring new technology on stream. Also, we have to predict what it will cost to transfer this new knowledge from the laboratory to the field or factory.

7. *Benefit/cost ratio for each new technology.* — Step 5, which gave us the 1980 benefits, over step 6, which gave us the cost of the new technology, gives us the benefit/cost ratio. If differing time periods will be involved among possible alternatives, we'll want to discount the streams of benefits and costs before we compare alternative investments.

8. *Estimate demand for cotton in 1980.* — After all possible new technologies for the various operations in production, marketing, etc., have been evaluated, we can begin to see what will happen to demand and price relationships. It may require several successive iterations before one can achieve a stable estimate for demand and price, the reason being that volume, costs, and prices are so interrelated.

9. *Evaluate consequences of adopting new technologies.* — What happens when yields are doubled? Can we sell twice as much cotton? What do we do with unneeded acres? What happens to unneeded laborers and even unneeded farmers? These are just a few of the consequences we need to think about that were overlooked in the past.

10. *Determine the priority for each research activity.* — Only at this stage are we ready to make decisions, and these must be based on several criteria — not just the benefit/cost ratio. We have to consider:

1. Benefits in relation to costs.

2. Extent research meets our goals.
3. Contribution to knowledge.
4. Urgency.
5. Scope and distribution of the benefits.

Being more familiar with the production system and looking at production as the beginning point of the cotton system, we began our analysis with the production subsystem. Our work or cost breakdown looked like this:

1. Land charge.
2. Residue disposal.
3. Land preparation.
4. Fertilizing.
5. Planting (includes seed and disease control).
6. Weed control.
7. Insect control.
8. Irrigation.
9. Harvest and haul.
10. Ginning.
11. Custom services.
12. Overhead labor.

At this point I must say that we haven't completed our systems analysis of cotton research. We hit a snag after completing the production research analysis. Our predictions made our economists very uncomfortable. Predicting a supply schedule was what made them uneasy. First, our productivity gains fell outside their trend lines. Then what to do about allotments control, price supports, and so forth. You must admit that what you assume about these factors could have a big impact on the outcome. We had to resolve our differences over what to assume before the analysis could proceed into the marketing part of the cotton system. One way out of this dilemma was to look further ahead, say to 1986, when we could begin to believe that all the necessary changes might be possible. Perhaps we can establish a trend and plot back to our position in 1980. Now that we're back on the track in our analysis, I'd like to review briefly our tentative findings in the production subsystem.

BENEFITS FROM PRODUCTION RESEARCH

First, the overall reduction in cost of production was estimated to be 11.1 cents per lb. of lint. What are the principal operations where we saved?

1. Land preparation and residue disposal — 1 cent.

2. Fertilizing — 1 cent.
3. Planting — 1/2 cent.
4. Weed control — 2.8 cents.
5. Insect control — 1.7 cents.
6. Irrigation — 1/2 cent.
7. Harvest and haul — 1.5 cents.
8. Ginning — 1.5 cents.
9. Other 4 operations together and round errors — 1.6 cents.

The 1966 cost, including land charge, was 26.9 cents. Less 11.1 cents = 15.8 cents per lb. of lint and associated seed.

What are the consequences of such a cost reduction? Optimistically, a net price of 12.5 cents per lb. of lint might bring forth a demand for 16 million bales in 1980. However, we'd make part of the price reduction through a 66-percent increase in yield as we do the production operations better. Even with 16 million bales, we'd need

some 2 million fewer acres harvested than the 9.6 million we had in 1966. There would likely be large regional shifts in production. Perhaps a loss of 0.8 million acres in the High Plains, and a 1/2 million each for the southeast and the blacklands-rolling plains. The Delta would gain a 1/2 million and the Far West a 1/4 million acres.

I hasten to point out that these estimates are highly tentative at this stage. However, let us not be complacent. Even if we make all the cost reduction gains that we think are possible, the cotton production industry is in for some great changes. We must be prepared to make the necessary adjustments. We need to do a better job of helping people make these adjustments. It's where we've done a very poor job in the past.

We still have the marketing, spinning and weaving, finishing and manufacturing subsystems to analyze. However, I don't look for our consequences problems to be solved in those areas. We face very stiff competition from the man-made fibers. It will be a hard fight and the consumer will reap the benefits.

It has been a pleasure to have this opportunity to tell you what we are doing. I hope we'll be able to help the industry pinpoint their most promising opportunities. Your task is a demanding one and we need to put our greatest emphasis on the most promising opportunities.

**COMPARISON OF STRUCTURES AND PROPERTIES OF COTTON CROSSLINKED
BY PAD-DRY-CURE, MILD CURE, POLY-SET, AND WET-FIX PROCESSES I.
PHYSICAL PROPERTIES OF FIBERS, YARNS, and FABRICS
[SUMMARY]**

by

James N. Grant, Frederick R. Andrews, and Louis C. Weiss
Southern Utilization Research and Development Division
New Orleans, La.

(Presented by James N. Grant)

Several commercially promising durable press processes for cotton, pad-dry-cure,¹ mild cure,² poly-set,³ and wet-fix,^{4,5} were examined for mechanism differences that might be responsible for variations in durable-press properties. This investigation was designed to study changes in chemical and physical properties of treated samples as the crosslinks are formed by the four durable-press processes.

Scoured fabric samples woven from Deltapine cotton were treated with the polyfunctional crosslinker, dimethyloldihydroxyethyleneurea (Permafresh 183) in all four processes. A proprietary resin, indicated to be primarily a methylated melamine formaldehyde (Aerotex 23S), was a component of the solution for the wet-fix process. Magnesium chloride hexahydrate was the principal catalyst during the cure for the pad-dry-cure, poly-set, and wet-fix processes. Mild cure process, a low

temperature cure, required the more active catalyst, hydrochloric acid. Zirconium acetate was the catalyst in step 1 of the poly-set process. These differences in catalysts and reagents were essential to the different processes, hence unavoidable. The fabrics were treated under conditions that would give acceptable durable-press properties. In practice, other reagents are employed in some of the processes which result in slightly higher crease recovery angles and durable-press ratings.

Kiered yarns were treated with the reagents and by the processes used for the fabrics. Yarn specimens were taken at time intervals during the fixation of crosslinks. The highest bound nitrogen for yarn of each process corresponded with the bound nitrogens for the fabrics. Procedures used to crosslink the yarns are described briefly in table 1. Physical properties of the yarns are discussed in this report, the chemical properties being given in other reports.

¹Vail, S. L., Murphy, P. J., Jr., Frick, J. G., Jr., and Reid, J. D. Dihydroxyethyleneureas as wrinkle-resistance finishing agents for cotton. *Amer. Dyestuff Rptr.* 50: 550-553. 1961.

²Reinhardt, R. M., Cashen, N. A., and Reid, J. D. A mild cure process for wrinkle-resistant cotton fabrics. *Textile Chem. Color.* 1: 415-422. 1969.

³Reeves, W. A., Hamalainen, C., St. Mard, H. H., and Cooper, A. S., Jr. Poly-set process for producing durable-press cotton goods. *Textile Res. Jour.* 37: 76-88. 1967.

⁴Hollies, N. R. S., and Getchell, N. F. Wet-fixation process for improved durable-press cotton. *Textile Res. Jour.* 37: 70-76. 1967.

⁵Vail, S. L., Young, A. H. P., Verburg, G. B., Reid, J. D., and Reeves, W. A. DP via wet-fixation. Part 1. Conditions during fixation. *Textile Indus.* 313(15): 184, 186, 189, 191-192, 194-195. 1967.

Table 1. — Procedure for crosslinking cotton yarns

Process	Reagent	Drying fixation	Cure
Pad-dry-cure	Permafresh 183	11 min. 82° C.	1 to 5 min. 160° C. ¹
Mild cure	Permafresh 183		4 to 13 min. 60° C. ²
Poly-set	Permafresh 183	11 min. 82° C. 1 to 5 min. 160° C. ³	3 min. 160° C. ¹
Wet-fix	Permafresh 183 and Aerotex 23S	1 to 24 hr. 21° C.	4 min. 160° C. ¹

¹Catalyst magnesium chloride hexahydrate

²Catalyst hydrochloric acid

³Catalyst zirconium acetate

Treating conditions needed to reach levels of crosslinks for durable-press properties varied with the processes. Bound nitrogen at durable-press level varied by at least threefold between the poly-set and wet-fix processes. Within a process, bound nitrogen was usually nonlinearly related to the time interval. During the initial intervals for the poly-set and wet-fix, the bound nitrogen increased rapidly but in these intervals for mild cure, the bound nitrogen increased slowly. Bound nitrogen increased rapidly during the final interval for the mild cure process. The levels of bound nitrogen are similar in steps 1 and 2 for dual step processes but physical properties of samples are extremely different.

At levels of crosslinking for durable-press properties, strength decreased to essentially equal levels in both yarns and fabrics. At stages during the crosslinking, the relationship of bound nitrogen to tenacity was inverse. If nitrogen was expressed as a fraction of that at

durable-press level in each process, the relationships to tenacity differ with processes as did the time intervals during the treatment. In mild cure, the small changes in tenacity during the early stages could be attributed to both the moisture and the low temperature associated with evaporation of water from the wet sample. The presence of moisture during fixation could be responsible for the high wet crease recovery for the fabric. In the poly-set and wet-fix yarns, tenacity decreased rapidly in the short time intervals, and changes in tenacity were small as durable press was approached. The wet-fix yarns show that the largest strength loss occurs below the level of durable press and that yarn strengths have small increases with the added resin.

At two levels of nitrogen, one below and the other at the level for durable press, tenacities of single fibers were higher than were those of yarns from which they were taken. Elongations for fibers and yarns were essentially equal. At the two nitrogen levels in each process, the tenacities and elongations were essentially equal except for mild cure samples. The low strengths at both nitrogen levels indicated that the strength loss plateau had been reached and that the major losses had occurred in the shorter intervals during treatment. It was in the interval immediately below the level of durable press for mild cure that the major strength losses occurred. At durable press levels, single fiber tenacities could be related to the processes. The small changes in secant modulus resulting from changes in tenacities and elongations show that possibly swelling and structural bonding differences could exist among the processes. Moisture regains and cellulose densities show differences in swelling, resin deposition, and catalyst entrapment.

The ability of single fibers to recovery from straining was increased by each process but not in equal amounts. The smallest increase was found in fibers of wet-fix treatment. The recovery at durable-press levels was high for fibers from each of the other processes. At the level below durable press, the recovery for fibers from the mild cure had not improved over that of the kiered. The small increase in recoverability for wet-fix is consistent with the small losses in strength and elongation and the high abrasion resistance reported for fabrics with this treatment. The high crease recovery for fabrics with low fiber recovery lead to concept of intra fiber bonding and interfiber crosslinking for the wet-fix process.

COMPARISON OF STRUCTURES AND PROPERTIES OF COTTON CROSSLINKED BY THE PAD-DRY-CURE, MILD CURE, POLY-SET, AND WET-FIX PROCESSES

II. SWELLING BEHAVIORS IN CAUSTIC SOLUTION

[SUMMARY]

by

Edith Honold and James N. Grant
Southern Utilization Research and Development Division
New Orleans, La.

(Presented by Edith Honold)

Caustic solutions of mercerizing strength react with chemically modified cottons insofar as the intrafiber regions are accessible to the alkali and space is available to accommodate the expanding structure. The interspersed chemical modifies the size and shape of the intrafiber spaces and a crosslinking reagent may alter the degree of accessibility to and the mobility of the cellulosic elements of the fiber. Any intrafiber change that restricts fiber expansion modifies the effectiveness of certain subsequent treatments whose success depends upon swelling the cotton, for example, aftermercerization.

Fiber swelling can be measured by the alkali swelling centrifuge test in terms of sorption from a 15-percent sodium hydroxide solution (w/w) when specified test conditions are maintained.¹ The alkali centrifuge value (ACV), (the percent increase in weight of the test specimen) is a numerical value that permits quantitative comparisons of the sorptivities or the swelling abilities of the cottons — both native and after modification with chemical reagents. It was shown previously that variability in ACV's and related properties depended upon the process whereby formaldehyde crosslinks were introduced into cotton samples, as well as upon the extent of the reaction.²

In this report, sorption data are reported for cotton-yarn samples that had been crosslinked with dimethyloldihydroxyethylenurea (Permafresh 183) by the pad-dry-cure, mild cure, poly-set, and wet-fix processes, and with Permafresh in conjunction with a proprietary resin that is indicated to be "primarily a methylated melamine formaldehyde" (Aerotex 23S) by the wet-fix process. Each group consists of samples cured or fixed for different periods of time culminating in that

time interval recommended for the preparation of smooth-drying cotton fabrics. The details of the preparations are given in Part I.³ For the alkali centrifuge test, the yarns were cut into 1/2 to 1 inch segments to minimize the external restraint to swelling that yarn twist can impose.¹

The ACV's for the crosslinked samples ranged from 260 to 160 as compared with an ACV of 253 for the noncrosslinked control. The relationship between percent nitrogen (representative of reagent content) and ACV can be generalized as a modified "lazy S" curve. All three groups treated with Permafresh alone combined to form the initial descending trend to a minimum ACV (about 215) in the region of 0.5 percent nitrogen and to start the ascending trend. Thereafter, the groups reached maxima at different levels and followed individual descending curves. The wet-fix curve was similar but displaced toward higher nitrogen and lower ACV. These alterations in ability to sorb the caustic solution reflect changes in intrafiber structure effected by the varying contents of reagent or reagents; the divergences among the groups show the influence of the preparatory processes.

Moisture regains are related to the availability of sites for the adsorption of water molecules. Two opposing alterations in intrafiber spaces, and, therefore, intrafiber surfaces, can be envisioned — a reduction caused by the presence of or the binding action of the crosslinking molecule and an expansion caused by the separation of cellulosic elements by the crosslinks. In the pad-dry-cure samples, the reduction presumably predominated since the moisture regain became progressively less as the reagent content increased. In the poly-set samples, the composite

¹Honold, E., and Grant, J. N. Cotton character test—the alkali swelling centrifuge test. *Textile Indus.* 133(1): 93, 95, 97, 100, 102, 116. 1969.

²Honold, E., Rowland, S. P., and Grant, J. N. Sorption of caustic solution by formaldehyde-crosslinked cottons. *Textile Res. Jour.* 39: 1023-1030. 1969.

³Grant, J. N., Andrews, F. R., and Weiss, L. C. Comparison of structures and properties of cotton crosslinked by the pad-dry-cure, mild cure, poly-set and wet-fix processes. I. Physical properties of fibers, yarn and fabrics. Pages 7-8 this proceedings.

change was negligible since the moisture regain value was maintained at a level close to that of the control. In the mild cure and the wet-fix samples, there was a shift in the dominance of the two factors with increasing reagent content. At 0.7-percent and 1.0-percent nitrogen, respectively, the maximum regains were about 1/2-percent-unit higher than that of the control.

Standard equilibrium moisture regains were redetermined after the tested specimens had been neutralized, washed, recentrifuged, and dried. These post-test regains are related to the degree of mercerization resulting from the action of the caustic solution. The regains of all the crosslinked samples were higher than that of the mercerized noncrosslinked control. The poly-set group had an average increase of 1.5 percent-units and the other three groups were indistinguishable with an average increase of 0.8 percent-unit. Presumably, the interspersed molecules of

the reagent prevented the normal realignment of the disrupted Cellulose I into the Cellulose II configuration and an augmentation of disordered regions resulted.

In these four groups of samples, the crosslinked reagent was partly removed by the caustic solution during the alkali centrifuge test and subsequent manipulations. On the basis of nitrogen percentages, the greatest loss occurred in those samples in all groups that originally had about 0.8 percent nitrogen. On the basis of formaldehyde percentages, the greatest loss occurred at different formaldehyde contents in the original samples in the order of 0.7 percent HCHO (poly-set), 0.9 percent (pad-dry-cure), 1.4 percent (mild cure), and 1.8 percent (wet-fix).

Crosslinking with Permafresh 183, alone or in combination with Aerotex 23S, and the partial removal of the reagents by the caustic solution during the alkali centrifuge test appear to be of a very complex nature.

COMPARISON OF STRUCTURES AND PROPERTIES OF COTTON CROSSLINKED PAD-DRY-CURE, MILD CURE, POLY-SET, AND WET-FIX PROCESSES. III. STRUCTURAL CONSIDERATIONS OF THE CROSSLINKED CELLULOSES [SUMMARY]

by

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(Presented by S. P. Rowland)

It has become increasingly evident in recent years that the superficially simple finishing of cotton fabrics with chemical reagents involves an exceedingly intricate interplay of the chemistry of the chemical reagent and the physics of the cotton fiber. *One approach* to a better understanding of the chemical and physical events that occur during different processes of crosslinking of cotton involves measurement of the number of effective crosslinkages (17) and determination of the structure of the reagent residues (11, 13). Such studies of cotton modified with tris(1-aziridinyl)phosphine oxide (11, 13, 17), with tris(2-chloroethyl)-phosphoramidate (9), or with sodium N-methylbis(2-sulfatoethyl)amine and N-methylbis(2-chloroethyl)amine (10, 12, 16) have shown that there is substantially less development of simple crosslinkages (i.e., single reagent units covalently bonded at each end to a cellulose chain) than had been hitherto believed. A substantial fraction of the crosslinking agent is found in the form of simple substituent groups (10), or "complex structures" which may include long crosslinks, long substituents (6), and resin deposited in the cotton with little or no covalent bonding to the cellulose (17).

The foregoing type of approach is dependent upon the development of linkages between reagent and cellulose and between units of reagent which are stable in the presence of strong base and strong acid. This is essential because cupriethylenediamine hydroxide (cuene), which is employed in the determination of the number of effective crosslinkages (15), is a strong base and because the isolation of structural components (before identification and quantitative determination) is dependent upon the acid catalyzed degradation of the molecular chain of cellulose to substituted and crosslinked glucose units. Unfortunately, reagent residues from N-methylol reagents, which are employed in the commercial processes for modification of cotton cellulose, are indicated to be quite sensitive to both base and acid (1). Therefore, the structures of reagent residues in cotton modified with these chemicals must be studied by less direct means.

A *second approach*, which is applicable to cottons treated with N-methylol reagents, is necessarily less direct. This involves factors such as (a) consideration of the composition of the reagent residues in terms of the $\text{CH}_2\text{O}/\text{N}$ ratio in the cotton, (b) assessment of the

proportion of reagent residues which are unattached or weakly attached to the cellulose, (c) estimation of the relative extent of crosslink development, and (d) evaluation of the uniformity of distribution of crosslinkages in the cotton.

In bringing emphasis to bear on the extent of crosslink development and the structure of the reagent residues, it is important that proper consideration be given to the location of the crosslinkages in the gross structures of the fabric and fiber. Observations made in studies of preferential crosslinking (that is, application of the reagent to one side of a fabric) give some clues as to what might be expected as a result of unintentional variations of this type in distributions of crosslinkages in the fabric (2). The importance of distribution of crosslinkages at the fiber level is emphasized by results which show that the higher level of wrinkle recovery, at a given level of retention of strength and abrasion resistance, is associated with the more homogeneous distribution of crosslinkages throughout the cross section of the fiber (5).

The present study of cotton chemically modified with N-methylol reagents by the pad-dry-cure process (3), by the mild cure process (8), by the poly-set process (7), and by the wet-fix process (4) involves the second type of approach. The essential features of each of these reactions are summarized in table 1 of Part I of this series of papers.

Evidence regarding the distributions of crosslinkages in the fibers of these modified cottons was obtained from electron micrographs showing the effect of cuene on thin cross sections of fibers (14), by characterization of the pattern developed in electron micrographs of thin cross sections after subjecting the fiber to the methacrylate expansion technique (14), by an adaptation of the sol-gel analysis (6), and by a detailed study of the progressive changes in swelling of the gel fraction throughout the course of the crosslinking reactions. The electron micrographic methods applied to cross sections of fibers showed little or no evidence of preferential developments of crosslinkages in peripheral regions of the fibers. However, the latter two methods noted above indicated the existence of significant differences among the cottons crosslinked by the various processes.

The compositions of the reagent residues, in terms of the ratio of formaldehyde (moles) to nitrogen (gram atoms), were found to be quite different among the final cured fabrics resulting from the various processes of crosslinking. The progressions of these ratios throughout the course of each of the finishing processes were even more pronounced in their individualities. In none of the processes was the composition of the reagent residues constant throughout the fixation or curing or both reactions.

Reproducible fractions of the reagent residues were found to be extractable from the finished fabrics resulting from each of the crosslinking reactions and from each one of the partly reacted samples resulting from less-than-complete fixation or cure. Cuene was the extracting agent. Soluble nitrogenous and formaldehyde components were readily removed from the cuene-swollen cellulose.

The extractable fractions of reagent residues ranged from approximately 15 to 70 percent of the total "bound" reagent. The development of extractable reagent residues during the course of the fixation or cure steps or both was uniquely characteristic for each of the processes of crosslinking.

A detailed consideration and analysis of data of the type noted above for the fabrics finished in the four different processes are bases for conclusions that the critical structural features that distinguish the cottons crosslinked by the wet-fix process are (1) a highly uniform distribution of crosslinkages throughout the fibers, (2) a high level of development of crosslinkages in a fiber structure which is relatively open or noncollapsed, and (3) a high level of stable bond development (stable to base) between cellulose and the nitrogenous reagent residues.

Literature Cited

1. Andrews, B. A. K., Arceneaux, R. L., Frick, J. G., Jr., and Reid, J. D. 1962. *Textile Res. Jour.* 32: 489-496.
2. Cooper, A. S., Jr., Walker, A. M., Hoffman, M. J., and Reeves, W. A. 1968. *Amer. Dyestuff Rptr.* 57: 1031-1035.
3. Frick, J. G., Jr., Kottes, B. A., and Reid, J. D. 1959. *Textile Res. Jour.* 29: 314-322.
4. Hollies, N. R. S., and Getchell, N. F. 1967. *Textile Res. Jour.* 37: 70-76.
5. Joarder, G. K., Brannan, M. A. F., Rowland, S. P., and Guthrie, J. D. 1969. *Textile Res. Jour.* 39: 49-54.
6. Joarder, G. K., and Rowland, S. P. 1969. *Textile Res. Jour.* 39: 247-253.
7. Reeves, W. A., Hamalainen, C., St. Mard, H. H., and Cooper, A. S., Jr. 1967. *Textile Res. Jour.* 37: 76-88.
8. Reinhardt, R. M., Cashen, N. A., and Reid, J. D. 1969. *Textile Chem. Color.* 1: 415-422.
9. Roberts, E. J., Brannan, M. A. F., and Rowland, S. P. 1970. *Textile Res. Jour.* (in press).
10. Roberts, E. J., Brannan, M. A. F., and Rowland, S. P. 1970. *Textile Res. Jour.* (in press).
11. Roberts, E. J., and Rowland, S. P. 1970. *Textile Res. Jour.* (in press).
12. Roberts, E. J., and Rowland, S. P. 1970. *Canad. Jour. Chem.* (in press).
13. Roberts, E. J., Wade, C. P., and Rowland, S. P. 1970. *Textile Res. Jour.* (in press).
14. Rollins, M. L., and Tripp, V. W. 1963. In "Methods in Carbohydrate Chemistry," Vol. III, R. L. Whistler, Ed., New York, Academic Press, p. 356.
15. Rowland, S. P., and Post, A. W. 1966. *Jour. Appl. Polymer Sci.* 10: 1751-1761.
16. Rowland, S. P., Roberts, E. J., and Brannan, M. A. F. 1970. *Textile Chem. Color.* (in press).
17. Rowland, S. P., Roberts, E. J., and Stark, S. M., Jr. 1970. *Textile Res. Jour.* (in press).

EFFECT OF TEMPERATURE ON THE INFRARED ABSORPTION OF CELLULOSICS [SUMMARY]

by

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(Presented by E. R. McCall)

Recently several investigators have obtained the infrared spectra of carbohydrates at lowered temperatures (1, 4, 8). Sharpening of bands, increase in intensity, and some frequency shifts are the most obvious changes that occur in the spectra obtained at low temperature. In an attempt to evaluate molecular bond character in cellulosic materials, a study was made on the effect of temperature changes on their spectra. The more significant changes observed in the spectra of *Valonia ventricosa* cellulose, hydrocellulose I (from cotton) and hydrocellulose II (from regenerated cellulose) at liquid nitrogen temperatures are described in this report.

On cooling, significant changes in both intensity and frequency were observed in the spectra of the celluloses in the OH stretching region. The absorption bands in this region at ambient and liquid nitrogen temperatures are listed in table 1. The general absorption in this region shifts to a lower frequency on cooling and the low temperature spectra are better resolved. Little change in intensity and no change in frequency occurs in the CH stretching region around 2900 cm^{-1} .

Table 1. — Effect of temperature in OH stretching region

Sample	Cellulose I		Valonia		Cellulose II	
Temperature	Ambient	Liquid N ₂	Ambient	Liquid N ₂	Ambient	Liquid N ₂
	—	—	—	—	3500	3500
	—	—	—	—	3460	3445
	3420I ¹	3410	3419	3410	—	—
	—	—	3388I	3377	—	—
Frequency	3355	3335	3364	3349	3365I	3340
(cm^{-1})	3305I	3280I	3324I	3307	—	—
	—	—	3288	3267	—	—
	—	—	3252	3231	—	—
	—	—	—	—	3168	3145

¹Inflection.

The shift to lower frequency in the OH stretching region indicates increased intermolecular hydrogen bonding. As a result, the nominal force constant of the OH bond is lowered, and less energy is required to cause the OH stretching vibration to occur. X-ray diffraction data have shown that a large lattice contraction occurs on cooling carbohydrates (1). Such a contraction, if it also occurs on cooling cellulose, would help to account for the increased intermolecular bonding.

Cellulose from the marine alga *Valonia ventricosa* is a highly crystalline, well oriented form of cellulose whose disordered fraction has been estimated to be about half that of cotton cellulose (7). This property makes it ideal for obtaining well resolved spectra of cellulose as evidenced by the large number of bands listed in the tables for *Valonia*. The changes that occur on cooling samples of hydrocellulose I and *Valonia* are similar even though the resolution is much greater for the latter.

Three absorptions in the spectrum of hydrocellulose II, which shift to a lower frequency on cooling were noted below 3500 cm^{-1} . However, a band at 3500 cm^{-1} does not shift when the sample is cooled. Zhbakov (8) has suggested that intramolecular hydrogen bonding is less affected by temperature than intermolecular hydrogen bonding. On the basis of these reports, the absorption at 3500 cm^{-1} is believed caused by a vibration from intramolecularly bonded hydrogen. Although the band at 3460 cm^{-1} at ambient temperature falls within the range reported for intramolecular hydrogen bonding, the relatively large shift (15 cm^{-1}) that occurs on cooling would indicate that this band is caused by an intermolecular vibration. Some of the bands in the spectra of these three celluloses in the $1800\text{-}300\text{ cm}^{-1}$ region that shift or appear on cooling are summarized in table 2. Contrary to the shifts observed in the OH stretching region, a general shift to a higher frequency occurs in this region of the spectrum on cooling. The vibration just above 1400 cm^{-1} has been assigned by various authors to a CH_2 symmetrical bend (2, 3, 6). This band exhibits a

small shift on cooling. If a lattice contraction similar to that observed by X-ray on cooling carbohydrates occurs in cellulose, the OH on the CH_2 group would be involved in the increased hydrogen bonding. A resulting increase in the energy required for the CH_2 bending vibration would produce such a shift to higher frequency. This shift has also been attributed to rotational isomerism (8) or to internal rotation involving changes only in the positions of hydrogen atoms (1).

The large shifts (up to 25 cm^{-1}) in the $800\text{-}600\text{ cm}^{-1}$ region indicate that these vibrations are particularly temperature-sensitive. The absorption bands in this region are due to skeletal vibrations rather than to small atomic groupings. The position of these bands would therefore be greatly affected by any change in the skeleton or lattice of the molecule accompanying contraction on cooling.

Fewer changes occur in the spectrum of *Valonia* than in the spectrum of hydrocellulose I on cooling. The crystallinity ratio for hydrocellulose I calculated by the Nelson-O'Connor method (5) at ambient and liquid N_2 temperatures increases much more than the ratio for *Valonia* calculated under the same conditions. This greater increase in crystallinity on cooling parallels the larger number of changes that occur in the spectrum of hydrocellulose I at liquid nitrogen temperature.

The spectral changes observed on cooling all of these celluloses are continuous with change in temperature. This smooth continuous change of the spectrum indicates a lack of phase change.

All of the bands that shift on cooling have been assigned by various authors to some type of vibration which would be affected by changes in hydrogen bonding. Since absorption bands in the spectra of samples containing no hydroxyl groups, such as cellobiose octaacetate and cellulose triacetate, do not shift with specimen temperature over this range, the shifts that were observed on cooling are undoubtedly associated with hydrogen bonding effects.

Table 2. — Effect of Temperature in $1800\text{-}300\text{ cm}^{-1}$ Region

Sample	Cellulose I		Valonia		Cellulose II	
Temperature	Ambient	Liquid N_2	Ambient	Liquid N_2	Ambient	Liquid N_2
	1434	1439	1434	1437	1420	1425
	—	765	744	765	—	—
Frequency (cm^{-1})	700	725	708	725	703 ¹	7171
	664	672	668	672	670	673
	—	651	—	651	—	—

¹ Inflection.

Literature Cited

1. Katon, J. E., Miller, J. T., Jr., and Bentley, F. F. 1969. Carbohydrate Res. 10: 505-516.
2. Liang, C. Y. and Marchessault, R. H. 1959. Polymer Sci. 39: 269-278.
3. Marchessault, R. H. and Liang, C. Y. 1960. Polymer Sci. 43: 71-84.
4. Michell, A. J. 1968. Australian Jour. Chem. 21: 1257-1266.
5. Nelson, M. L. and O'Connor, R. T. 1964. Jour. Appl. Polymer Sci. 8: 1325-1341.
6. O'Connor, R. T., DuPre, E. F., and McCall, E. R. 1958. Textile Res. Jour. 28: 542-554.
7. Okajima, S. and Kai, A. 1968. Polymer Sci. Part A-1, 6: 2801-2817.
8. Zhbankov, R. G. 1969. Polymer Sci. Part C, No. 16: 4629-4643.

INVESTIGATION ON THE CHEMICAL STRUCTURE OF CROSSLINKED COTTON¹
[SUMMARY]

by

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(Presented by H. Zollinger)

The growing significance of easy-care cotton textiles in the last two decades is the result of endeavors to modify cotton *chemically* in order to increase its useful properties. A review of the work done during this period will show that the emphasis has been on the improvement of the textile mechanical properties of cotton by changing the chemicals applied, the application conditions, such as temperature, time, and catalysts, and the type of processes such as pad-dry-cure, wet-fixation, vapor-phase, and core/skin reactions. It seems that this approach, which is a largely empirical one, reached its optimum. Further improvements may be possible by carrying out fundamental research on the *molecular* causes of the favorable and unfavorable changes in textile mechanical properties of easy-care cotton. A prerequisite for such research is a detailed knowledge of the chemical constitution of the finished cotton.

Although it has long been assumed that *cross-linking* of the cotton is the basic cause of the changes observed, *qualitative* chemical proof has been furnished only in recent years. The *quantitative* elucidation of the structure of cross-linked cellulose now appears to be reaching a more fruitful stage by means of the application of physico-chemical and physical methods as well as degradative processes, that is, the methods used in organic chemistry.

EXPERIMENTAL

This paper is concerned specifically with the investigation of the chemical structure of cotton, "print cloth" fabrics, cross-linked by immersion in formaldehyde/water/acetic acid/hydrochloric acid mixtures (Form D and Form W type applications). In contrast to a previous investigation (b), reaction conditions were chosen so that the formaldehyde content of the treated fabrics was in the range of 0.2 to 1.0

percent (w/w of fabric), that is, concentrations of practical use. Formaldehyde was used for this investigation because it is the cheapest cross-linking agent and because it is the object of a research project² which is concerned with some unfavorable characteristics of formaldehyde finishes (relatively low reliability in application, lower resilience/strength and abrasion ratios than obtained with other cross-linking reagents).

Three series of different application mixtures were investigated. These were:

N-Series: 3.6 percent CH₂O, 3.7 percent HCl, 9 to 25 percent H₂O, rest CH₃COOH

H-Series: 7.5 percent CH₂O, 17.5 percent HCl, 9 to 70 percent H₂O, rest CH₃COOH

Z-Series: 3.6 percent CH₂O, 3.7 percent HCl, 18 percent H₂O, 74.7 percent CH₃COOH, reaction time

8 to 90 minutes, resulting in up-takes of 0.26 to 1/04 percent CH₂O.

In the N- and H-series, the reaction times were varied so that up-takes of 0.72 ± 0.05 percent and 0.80 ± 0.06 percent respectively were obtained. All applications were made at room temperature as described elsewhere (13) and the fabrics washed by the process already described (7).

RESULTS AND DISCUSSION

3.1 *Textile mechanical properties of the samples* — The textile mechanical properties of the three series are plotted in figures 1 to 3 as a function of percent CH₂O

¹Investigations in Textile Chemistry, Part XXI. Part XX of this series see O. Annen, K. Heinisch, M. Kimura, S. Kalyana Raman, H. K. Rouette, A. Wehner, H. Zollinger, *Textilveredlung* 5 (1970). [In press]

²In progress, in collaboration with the International Institute for Cotton.

(Z-series) and of percent H₂O in the application liquor (N- and H-series), respectively. We should like to emphasize that the goal of the present investigation was not to optimize the method of application or the reaction conditions with respect to resilience/strength, resilience/abrasion and similar ratios, but to obtain a series of comparable samples for the purpose of elucidating their chemical structure.

3.2 Chemical structure of the samples — The method of elucidating the chemical structure was in principle the same as before (permethylation, acid degradation to a mixture of methylated glucoses, hydrogenation to the respective derivatives of sorbitol, and VPC chromatography of their acetylated derivatives). This method had to be modified, however, because of low DS.

The percentages of the nine expected degradation products (2.3.4.6-tetramethylsorbitol, 2.3.6-trimethylsorbitol, 3.6-, 2.6- and 2.3-dimethylsorbitol, 2-, 3- and 6-monomethylsorbitol and sorbitol) are a measure firstly of the *relative apparent reactivities of the hydroxyl groups*³ in the 2-, 3- and 6-positions of the anhydroglucose units (AGU) of cellulose and, secondly, if we take into account the experimental values for the uptake of formaldehyde, of the *average chain length (n) of the cross-links*. Further evaluation of the data makes it possible to differentiate between the *intraglucosic* bridges, that is, bridges between two hydroxyl groups of the *same* AGU, and the sum of *intrachenar* and *intermolecular* cross-links⁴.

The percentage yields of these degradation products and additional analytical data such as (formaldehyde and methoxyl contents) will be given in detail later. Some essential results are summarized in table 1.

Table 1. — Summary of degradation results (Z-, N- and H-series)

Sample	Application Percent H ₂ O ₁	Duration min.	Percent CH ₂ O on fabric	Apparent reactivities C(2):C(3):C(6)	6-Mono- methyl sorbitol	Average chain length <i>n</i>
Z 1	18	8	0.26	0.11 : 0.09 : 1.0	0.15	1.4
Z 2	18	18	0.54	0.04 : 0.04 : 1.0	0.18	1.7
Z 3	18	32	0.79	0.03 : 0.07 : 1.0	0.20	2.4
Z 4	18	50	0.94	0.05 : 0.06 : 1.0	0.24	2.6
Z 5	18	90	1.04	0.06 : 0.06 : 1.0	0.30	2.6
N 9 ²	9	35	0.68(0.25)	0.05 : 0.09 : 1.0	0.15	1.5
N 18	18	50	0.70 ³	0.04 : 0.05 : 1.0	0.35	2.2
N 25	25	360	0.71	0.05 : 0.06 : 1.0	0.20	2.4
H 9	9	22.5	0.83	0.06 : 0.09 : 1.0	0.30	1.8
H 18	18	7	0.82	0.08 : 0.09 : 1.0	0.40	1.5
H 30	30	2.5	0.84	0.08 : 0.07 : 1.0	0.48	2.0
H 50	50	2.5	0.79	0.11 : 0.05 : 1.0	0.32	2.2
H 70	70	90	0.72	0.10 : 0.06 : 1.0	0.25	2.0
5104[A]	(4)	(4)	1.74	0.07 : 0.06 : 1.0	1.4	2.5

¹Percent H₂O in application mixture.

²This sample was degraded after 1 year of storage and a considerable loss of formaldehyde was found.

³Entries 24 and N18 show that formaldehyde uptake is difficult to achieve.

⁴Alkaline reaction product with CH₂(OSO₃H); see text.

³As formaldehyde is a bifunctional reagent, it is not possible to define *one* reactivity of a specific hydroxyl group to formaldehyde. The measured reactivities are average reactivities of the first and second step of formaldehyde/hydroxyl group reactivities. Therefore, they are called *apparent* reactivities, see also (7) and (13).

⁴For a definition of intraglucosic, intra- and interchenar, intra- and intermolecular bridges see footnote 3 in (7).

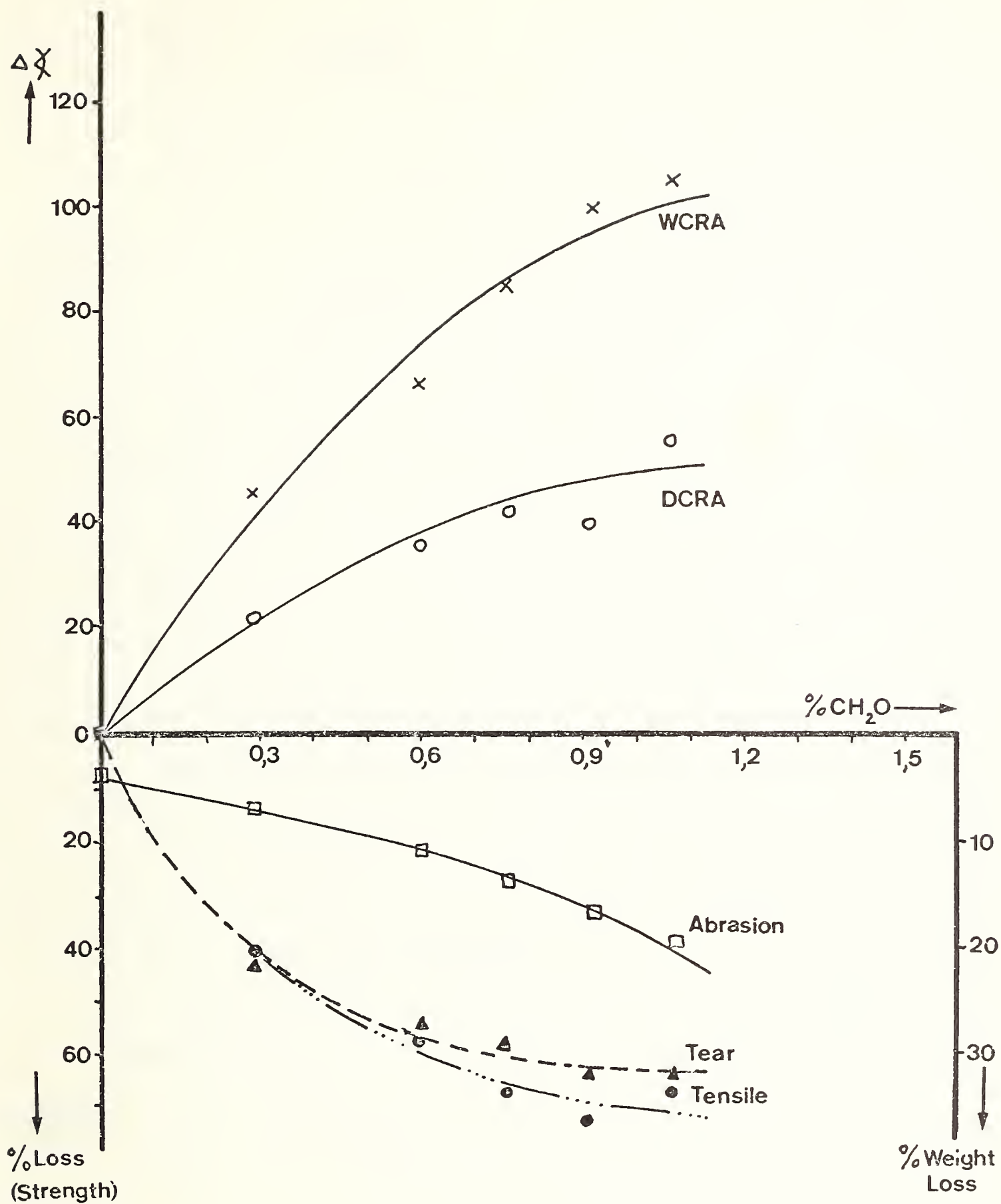


Figure 1: — Textile mechanical properties of the Z-series

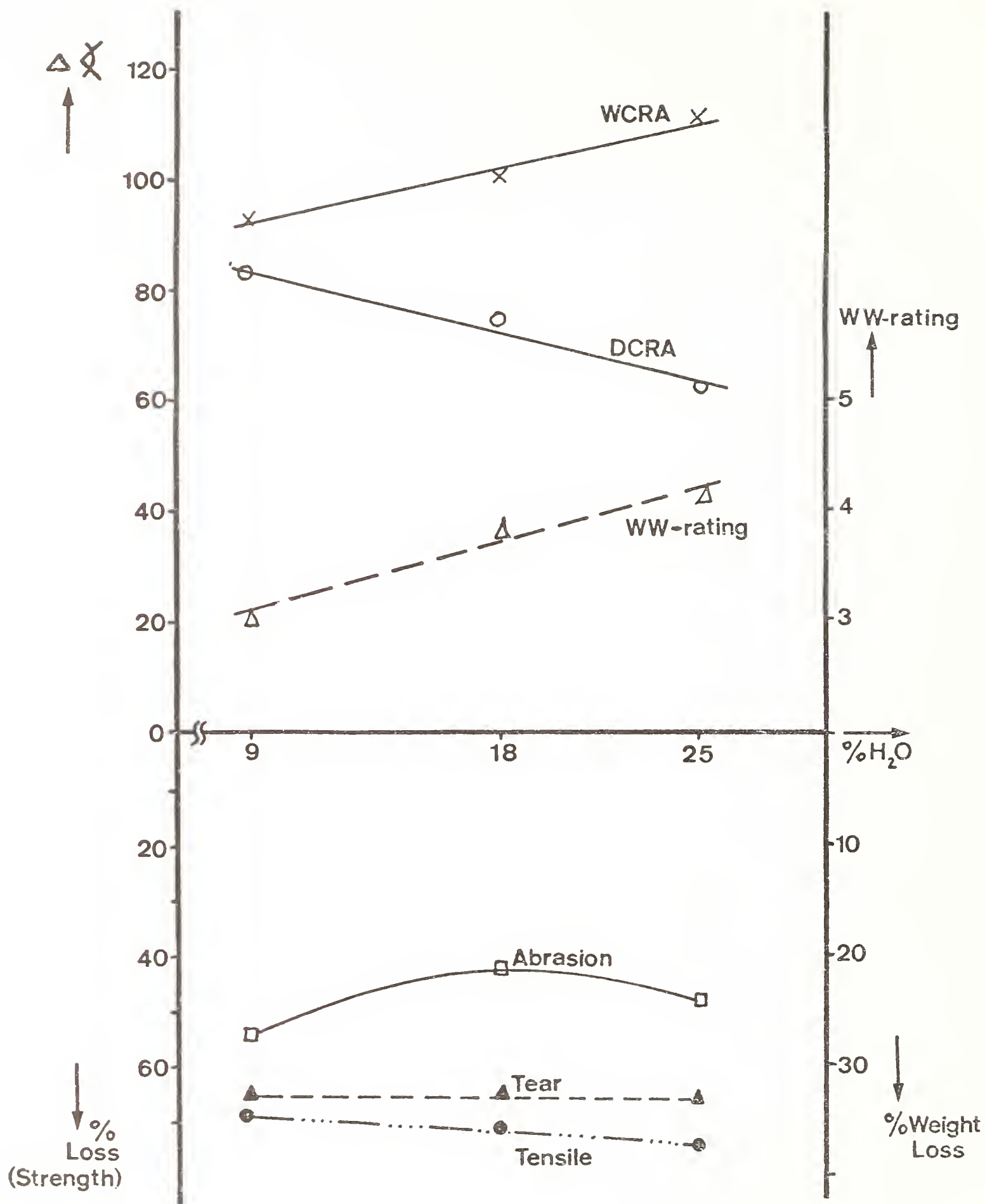


Figure 2. — Textile mechanical properties of the N-series

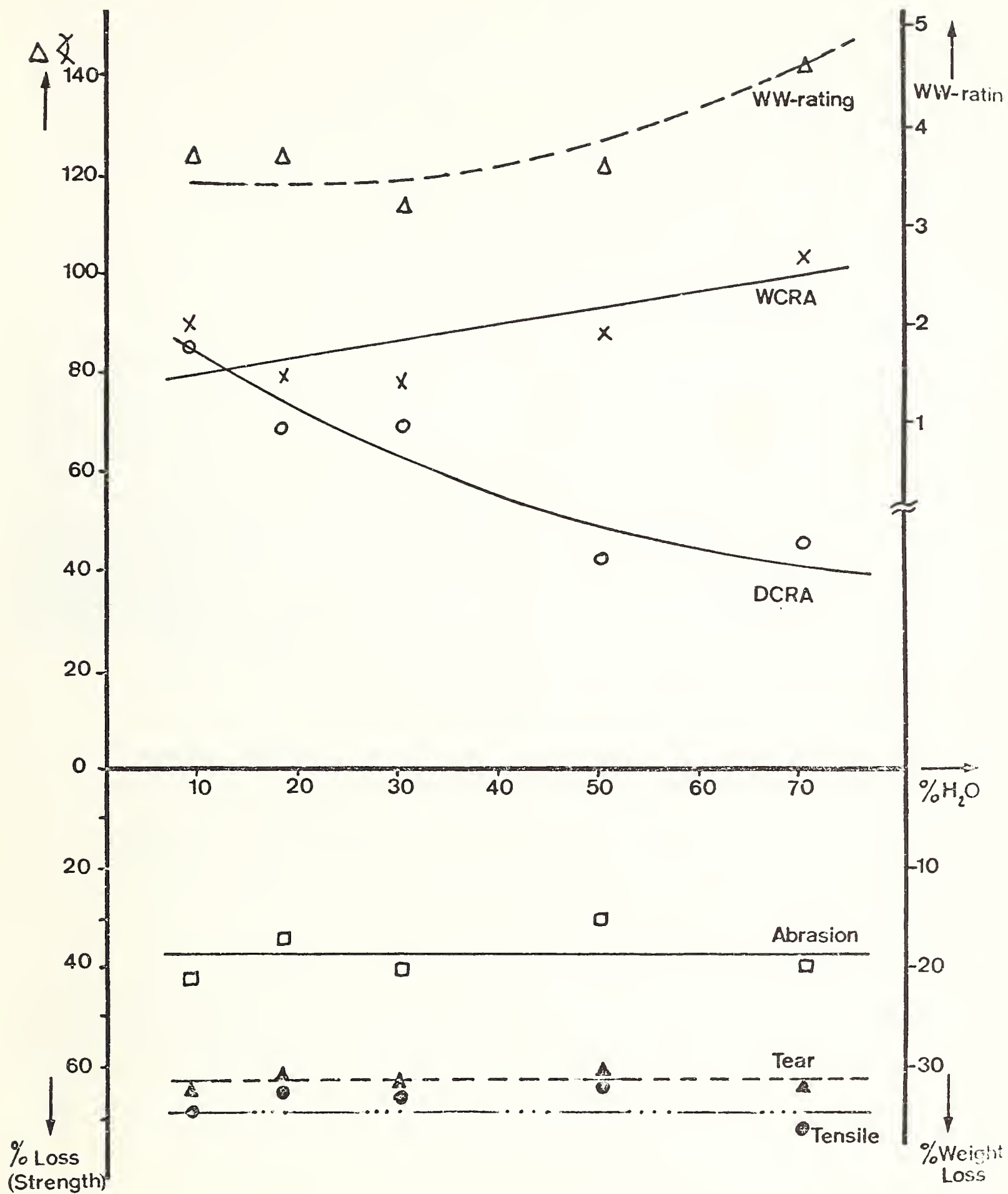


Figure 3. — Textile mechanical properties of the H-series

The apparent reactivities of the three hydroxyl groups are based on the ratio of the three isomeric dimethylsorbitols only. 6-Monomethylsorbitol is not considered for the apparent reactivity ratio for reasons given later.

It is interesting to note that in all these samples with low D.S., no 2- and 3-monomethylsorbitol and no sorbitol were found. This result should be contrasted with that reported in our previous paper (7). In that case, the samples had a D. S. which was normally four or more times higher (3 to 4 percent CH₂O on fabric).

Z-series: Rowland (9) demonstrated that the reactivity ratio of the three hydroxyl groups is different for reversible and irreversible reactions. The first step of formaldehyde cross-linking, the formation of O-methylol compounds (1), is fast and reversible (8), whereas the cross-linking proper (3) is slow, but also reversible. The formaldehyde uptake results for the Z-series demonstrate clearly that equilibrium is not attained after 90 minutes.



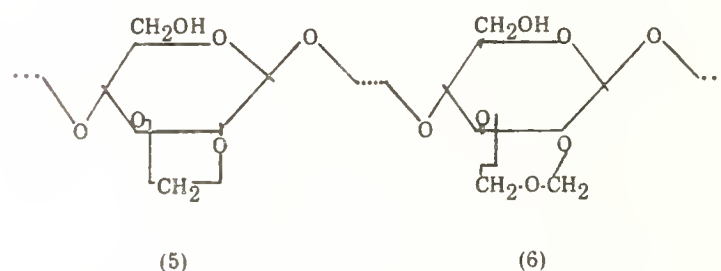
The apparent reactivity ratios can be best explained by assuming that the above reactions are reversible rather than irreversible. However, we must emphasize that other factors, in particular the rates of swelling and diffusion, the different affinities of *all* types of particles in the system with respect to cellulose (CH₂O, H₃O⁺, Cl[−], H₂O, CH₃COOH), accessibility of cellulose and (thermodynamic) activity of the mineral acid should also be considered.

The reversibility of the reaction is indicated by the increase in chain length with reaction time. It can be explained by the grafting reaction (4) and the consequent formation of cross-links of chain length *n*=2 in reaction (5). It is clear that products of chain length *n*=2 can be formed also by condensation of two O-methylol products of reaction (1). Subsequent grafting after reaction (4) would then yield cross-linked products with *n*>2.

Of particular interest is the fact that significant amounts of 6-monomethylsorbitol are found. Formally 6-monomethylsorbitol results from *one* AGU which was

cross-linked *twice* (in 2- and 3-position). A statistical calculation, however, demonstrates that, if reasonable assumptions on accessibility and reactivity are made, an AGU already substituted in 2- or 3-position will react again in the other position (3-, and 2-, respectively) about 100 times *less* frequently than we found experimentally. Even if it is assumed that an O-methylol group in the 2-position activates the hydroxyl group at C₃ by a factor of 2-4, as found by Rowland and others (11) and Cirino and others (2), one would have expected a percentage of 6-monomethylsorbitol which is at least 20 times smaller than that found experimentally. We conclude, therefore, that this degradation product is not due to double cross-linking at the same AGU, but to an intraglucosic bridge between these two positions. That reaction has a higher probability as the O-methylol group is already in a favorable steric position relative to the neighboring OH group of the *same* AGU.

The formation of such an intraglucosic bridge was suggested previously by Guthrie (4) on indirect evidence for cellulose reacted with methylenedisulphuric acid [CH₂(OSO₃H)₂] under alkaline conditions. Guthrie considered this bridge to be monomeric (*n*=1, formula 5). We find, however, with Dreiding and Stuart atomic models, that only dimeric or longer bridges (*n*=2, formula 6) are possible sterically. Our conclusion is supported by degradation results on the original sample 5104 [A] of Guthrie treated with methylenedisulphuric acid.⁵ Here the ratio of 6-monomethylsorbitol to the sum of the three isomeric dimethylsorbitols is three to four times higher. Under Guthrie's conditions, therefore, intraglucosic reactions are predominant. Intermolecular cross-linking takes place to a small extent only and little change in the textile mechanical properties is observed.



H- and N-series — Apparent reactivity ratios are little influenced by the water content of the application bath. As no increase in the relative reactivity of the 2- and 3-position is observed under higher swelling conditions (see, however, the work of Rowland and coworkers (11)), we conclude that in all our samples reaction takes place *on the surface* but not in the *elementary fibrils*. A similar surface reaction was suggested by R. Jefferies, J. G.

⁵Samples kindly supplied to us by J. D. Guthrie, SRRL, USDA, New Orleans, La.

Roberts, and coworkers (5) for the methylation of cellulose. Our conclusion is supported also by the kinetic investigation of Rowland, Rollins, and deGruy (12) who demonstrated that intrafibrillar reaction of cellulose with formaldehyde takes place only at higher formaldehyde uptakes than were used in our investigation. An interesting observation is the high reactivity of the OH group in 3-position relative to that in 2-position in all our samples. Tentatively we suggest that this is due to reversible breaking the intraglucosic 2.3-bridge between the 2-oxygen atom and the adjacent methylene group.

3.3 Correlation between Chemical Structure and Textile Mechanical Properties — In this paper, correlations of the chemical structure of cellulose formals with time and composition of the application bath are discussed.

We investigated also the influence of reaction rate, the catalytic activity of mineral acids in mixed solvents (acidity functions), the composition of the mixture in the fibres relative to that of the application bath and the swelling rate using a new and simple type of equipment (6). However, the influence of these parameters on the reactivity of cellulose/formaldehyde systems and on the textile mechanical properties are presented in another paper (1).

The apparent reactivities of table 1 indicate clearly that crosslinking proper with formaldehyde takes place preferentially between hydroxyl groups in 6,6'-position. Intraglucosic 2.3-bridges are formed but as they do not lead to an improvement of cotton performance properties, their formation should be avoided in formaldehyde application processes.

An important parameter is the average chain length n . It is evident from a comparison of the crease recovery angles and the chain length in series N and H that longer cross-links influence the wet crease recovery (WCRA) favorably, whereas shorter chain lengths result in improved resiliency of the conditioned fabric. The advantage of formaldehyde for such a study is the fact that, in contrast to N,N'-dimethylol compounds very short chains — one carbon atom between two cellulose hydroxyl oxygens — are available. Therefore, an increase of n from 1.5 to 2.4 clearly demonstrates an improvement in WCRA. At significantly higher values of n a decrease is to be expected in analogy to work by Clingman and Schwenker (3).

In our other recent investigation (1) we describe how the other parameters mentioned at the beginning of this paragraph influence the rate of reaction of formaldehyde with cellulose. It seems feasible to assume that knowledge of all these factors will allow a multifunctional optimization of the performance characteristics of cotton cross-linked with formaldehyde.

ACKNOWLEDGEMENT

This investigation was conducted under [P. L. 480 Project UR-E27-(20)-2]. We thank many coworkers of the Southern Regional Research Laboratory in New Orleans, La., in particular J. D. Guthrie, S. P. Rowland, and W. A. Reeves for helpful discussions and suggestions.

Literature Cited

1. Annen, O., Heinisch, H., Kimura, M., and others. 1970. *Textilveredlung* 5: [In press].
2. Cirino, V. O., Bullock, A. L., and Rowland, S. P. 1969. *Jour. Polymer Sci. A-1*, 7: 1225-1235.
3. Clingman, A. L., and Schwenker, R. F., Jr. 1965. *Jour. Polymer Sci. C11*: 107-118.
4. Guthrie, J. D. 1967. *Textile Res. Jour.* 37: 40-45; see also Gallagher, D. M. 1966. *Textile Res. Jour.* 36: 850-853.
5. Jeffries, R., Roberts, J. G., and Robinson, R. N. 1968. *Textile Res. Jour.* 38: 234-244; Haworth, S., Roberts, J. G., and Robinson, R. N. 1967. *Textilveredlung* 2: 361-365.
6. Kalyana Raman, S., and Rouette, H. K. 1970. *Jour. Textile Inst.* [In press].
7. Patel, S., Rivlin, J., Samuelson, T., and others. 1968. *Textile Res. Jour.* 38: 226-234.
8. Roff, W. J. 1959. *Textile Inst.* 50: T353-T372.
9. Rowland, S. P., Bullock, A. L., Cirino, V. O., and others. 1967. *Textile Res. Jour.* 37: 1020-1030; Rowland, S. P. 1969. *Amer. Dyestuff Rptr.* 58: 15-18, 41.
10. Rowland, S. P., Roberts, E. J., Bullock, A. L., and others. 1969. *Textile Res. Jour.* 39: 749-759.
11. Rowland, S. P., Roberts, E. J., and Wade, C. P. 1969. *Textile Res. Jour.* 39: 530-542.
12. Rowland, S. P., Rollins, M. L., and deGruy, I. V. 1966. *Jour. Appl. Polymer Sci.* 10: 1763-1776.
13. Zollinger, H., and coworkers. 1969. Final Technical Report, P. L. 480 Proj. UR-E27-(20)-2.

INFLUENCE OF THE CATALYST IN COTTON-EPOXIDE REACTIONS [SUMMARY]

by

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(Presented by J. B. McKelvey)

The modification of cotton cellulose by use of catalyzed epoxide solutions has been known since the first World War. The reagents are relatively inert toward cellulose without the aid of a catalyst. It was usually stated that acids, bases, and salts would open epoxide rings, but union of the group with cellulose is another matter. It is true that cases may be cited where any of the above catalytic systems cause addition to cotton, but no general or universal rule is at hand. The reasons for such erratic behavior may be due to hydrolysis of reagent, dimerization, side chain grafting, and steric considerations.

The present study shows that the simplest epoxide, ethylene oxide, does not add to cotton in presence of mineral acids, but does add readily in presence of salts, such as NaCl, or in the presence of fixed bases. In fact, if enough add-on is obtained, the cotton will become soluble in water or in sodium hydroxide solutions. The same may be said in the case of propylene oxide. However, this base catalyzed activity vanishes at C₅ - C₆ in the homologous series and higher 1, 2 epoxides are without action in such systems. Epoxide groups located in the interior of a chain or occurring on ring systems are inactive with cotton. Either the ring is too sensitive to catalysts or too inert to be of practical use.

About 1956 the Lewis acid catalysts were introduced, particularly the fluoborates of Zn, Cd, and Mg. These are latent catalysts which may be added to epoxide solutions and on heating evolve BF₃ which may complex with oxygen-containing compounds — epoxides included. Oxirane rings are said to be strained and readily opened. Sometimes union of the epoxides with cellulose occurs. The fluoborate catalysts were most effective with diepoxide compounds, many of which have been examined for production of resiliency in cotton fabrics. Monoepoxide additions to cotton with fluoborates have been relatively unsuccessful. However, epichlorohydrin in the vapor state has been added to cotton with fluoborate catalysis.

An example of a Lewis base catalyst is the urea — epichlorohydrin-cellulose reaction. Bases in general have been the subject of much investigation in this laboratory. The research has been quite productive and covers the formation of soda cellulose both in aqueous and nonaqueous solutions. Furthermore, many salts are alkaline in nature and even neutral salts become basic in the presence of epoxides in protic solvents

(psuedo-basicity). In these studies, we have relied on lower, more active epoxides such as epichlorohydrin

$$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ (\text{C}_1\text{CH}_2\text{CH}-\text{CH}_2) \\ \diagdown \quad \diagup \\ \text{O} \end{array} \quad \text{and} \quad \text{butadienediepoxides}$$
$$\begin{array}{c} \text{O} \quad \text{O} \\ \diagup \quad \diagdown \quad \diagup \quad \diagdown \\ (\text{CH}_2-\text{CH}-\text{CH}-\text{CH}_2) \\ \diagdown \quad \diagup \quad \diagdown \quad \diagup \\ \text{O} \quad \text{O} \end{array} \quad \text{d, 1 and racemic}.$$
These studies were largely aimed at the production of crease resistance in cotton fabrics.

Epichlorohydrin, when added to cellulose with sodium hydroxide as catalyst, affords only the wet variety of crease recovery. However, if other alkalies, such as ortho- or metasilicates, trisodium phosphate, or sodium azide, are used, resilience in the dry state can be obtained with cotton. Similarly, strong solutions of LiCl, NaCl, CsCl, or MgCl₂ give good results. Zn(BF₄)₂ will cause the addition of epichlorohydrin to cotton when the reagent is in the vapor state, but not in the liquid state.

In the case of the butadienediepoxide it has been found that the meso isomer is soluble only in the more dilute caustic (6 to 8 percent), but the d,1 isomers dissolve readily in 23 percent NaOH. The two rings seem to open with equal speed either in basic or Lewis acid medium. Using the d,1 mixture, it has been found possible to obtain dry wrinkle recovery in cotton even when it is treated in the wet swollen state. Either isomer will cause cotton to be very highly crease resistant in both wet and dry states when catalyzed with Zn(BF₄)₂. With Zn(BF₄)₂ only small weight gains, in the order of 1 to 2 percent gain, are required for wrinkle recovery angles of 300 (W+F) in both the wet and dry states.

Other bases, such as primary, secondary, or tertiary amines, also cause addition of epoxides to cotton when used as external catalysts — particularly with butadienediepoxide. A method of considerable promise has also been found in the already modified DEAE (diethylaminoethyl) cellulose. This cotton can be useful when the nitrogen content from the "built-in" tertiary amine is 0.5 to 1 percent. When such a fabric is contacted with hot epoxides, many of them add to the cotton. Epichlorohydrin in particular reacts readily and gives a fabric with wet and dry recovery at fairly low weight gains. Even some of the longer chain epoxides react in a sluggish fashion. The methods of preparation of DEAE cellulose have been improved several times. The latest preparation has been accomplished by using nonaqueous

“sodacell.” This type of DEAE cotton may be obtained with above 1 percent N by one treatment of “sodacell” with chloroethyldiethylamine.

Nonaqueous “sodacell” itself has been made by a modified Schwenker-Pacsu method in which the sodium

in sodium methoxide in methanol solution is exchanged with a hydrogen from cellulose hydroxyl. The material is washed, purified in t-butanol under N_2 , and stored in this solution safely for short periods of time. This alkaline material also serves as a reactant for various epoxides some of which did not produce good results in aqueous media.

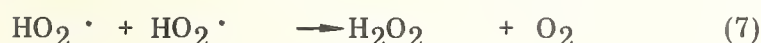
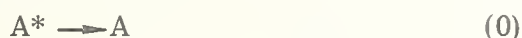
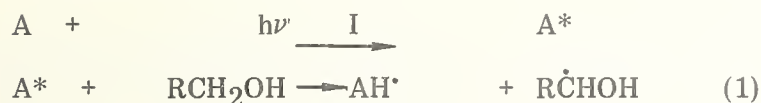
THE EFFECT OF LIGHT ON COTTON IN THE ABSENCE AND PRESENCE OF ANTHRAQUINONOID DYES [SUMMARY]

by

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Despite the fact that fading (4) and phototendering (8) vat dyed cotton have been extensively studied, there is no clear understanding of the mechanisms involved. Our studies were first carried out using model anthraquinone derivatives, where the structure is less complex than the vat dyes. The relevance of photochemical mechanisms established for these sensitizers to vat dyes on cotton was subsequently examined. On the basis of the mechanisms identified, photostabilising systems which can protect vat-dyed cotton from photodegradation are proposed.

Anthraquinone sulphonates. — For sodium 9, 10-anthraquinone 2-sulphonate and -2,6-disulphonate, when the concentration is in the region of 10^{-4} M, the photo-sensitized process can adequately be accounted for by the mechanism (1, 10):



where A represents the ground state and A* the photoexcited state of the sensitizer, AH[•] the corresponding semiquinone radical and RCH₂OH the carbohydrate. The photoexcited state A* reverts to the ground state only via reactions (0) and (1), giving effective kinetics represented by:

$$\begin{aligned} 1/(-d[RCH_2OH]/dt) &= 1/(-d[O_2]/dt) \\ &= 1/I + (1/I) \cdot (1/[RCH_2OH]) (k_0/k_1) \end{aligned}$$

where I = rate of activation, proportional to the intensity of light. On the basis of oxygen absorption measurements

or rates of product formation, there is a linear relation between 1/(initial rate) and 1/(RCH₂OH) from which (k_0/k_1) for any sensitizer or substrate may be calculated.

Flash photolysis and kinetic studies have shown that when the concentration of sensitizer (A) is increased, another process becomes significant (11):



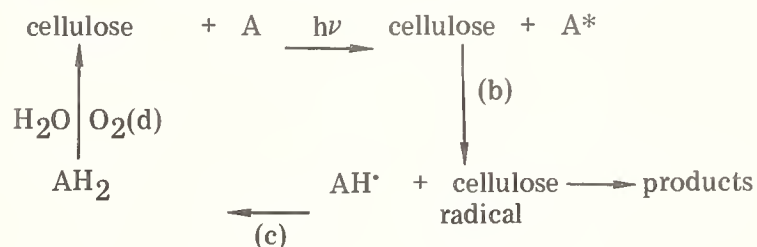
where A^{•+} is the semioxidized and A^{•-} the semireduced form of the sensitizer, related to the semiquinone (AH[•]) by the relationship



Reaction 9, independently of the cotton substrate, can give rise to coloured hydroxy-anthraquinone products, and hence destruction of the sensitizer (or dye). Moreover, these are also reactive intermediates, which are able to react to give radical species, that can initiate the phototendering process:



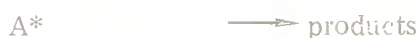
Using diffuse reflectance methods, we have demonstrated that such reactions also proceed when the sensitizers are present in monodisperse form on cotton cellulose (2), and the process may be represented:



Following the photo-activation reaction (a), the $\eta\pi^*$ state is able to initiate abstraction (b) as occurs in solution, giving a cellulose radical that leads to degradation. The semiquinone (AH[•]) in the ground or excited state (4) may abstract a hydrogen atom to yield the anthraquinone (AH₂) by reaction (c). Facile regeneration of the sensitizer by reaction (d) can be demonstrated. We have found that oxygen and water vapour are necessary for this step.

Vat dyes. — A competition between several processes following initial light absorption by the dye adequately accounts for our observations of fading and phototendering associated with vat dyes on cotton (3).

For nonaggregated dye (A) following light absorption, the following competition process may be envisaged:



where A^* and $(\text{cellulose})^*$ indicate excited states. Visible light would also promote the abstraction reaction.

When the dye is aggregated, the initial excitation may be dissipated additionally by



On the basis of these mechanisms, water and oxygen would, as we have found, exert a profound influence on the course of the reaction.

Direct photolysis. — The changes induced by short-ultraviolet radiation must be considered independently (8). Undoubtedly, a somewhat different mechanism operates, both in phototendering and in fading. Radiation of 253.7 nm will initiate direct

photolysis of cotton (8, 9) and the presence of vat dyes will reduce the extent of photodegradation (3). It is our view that direct photolysis by 253.7 nm arises not from a single chromophore but the absorption is associated with the entire hydrogen-bonded matrix. Diffuse reflectance measurements and semiconductor measurements demonstrate that exciton states of *ca.* 4 eV can be produced in high yield on irradiation of solidstate carbohydrates (6, 7). Direct absorption of light of this energy would, therefore, lead to photodegradation. Alternatively, degradation would accompany the transfer of the equivalent electronic energy from a closely associated molecule that absorbs that light. This latter path (reaction 14) is the most probable mechanism for the introduction of electronic energy into cellulose when vat dyed cotton is exposed to ultraviolet light. After initial absorption of 253.7 nm radiation by the vat dye, internal conversion from the $\pi\pi^*$ state to the $\eta\pi^*$ state would allow this state to participate in the abstraction reaction (13). Alternatively, the energy could be directly transferred to the cellulose (reaction 14) and initiate photodegradation. On this basis the dye which promotes greater phototendering would be the most efficient desensitizer to ultraviolet irradiation. This is found to be general behavior for the vat dyes (3).

Excited states. — The nature and reactivity of the excited states that promote the photosensitization reactions have been examined. Energy transfer processes to a suitable acceptor (Q):



can promote photostabilisation of the cotton cellulose, when reaction (17) proceeds efficiently in competition with reaction (14). Using pulse radiolysis the rate constants of such protective energy transfer processes have been studied (5). In this way good photostabilisers can be selected.

Literature Cited

1. Baugh, P. J., Phillips, G. O., and Arthur, J. C., Jr. 1966. *Jour. Phys. Chem.* 70: 3061-3069.
2. Baugh, P. J., Phillips, G. O., and Worthington, N. W. 1969. *Jour. Soc. Dyers Colour.* 85: 241-245.
3. Baugh, P. J., Phillips, G. O., and Worthington, N. W. 1970. *Jour. Soc. Dyers Colour.* 86: 19.
4. Giles, C. H., and McKay, R. B. 1963. *Textile Res. Jour.* 33: 528-577.
5. Hulme, B. E., Land, E. J., and Phillips, G. O. 1969. *Chem. Commun.*, p. 518.
6. Phillips, G. O. 1966. *In* "Current Topics in Radiation Research." Ed. by M. Ebert, 2: North Holland, Amsterdam.
7. Phillips, G. O. 1966. *In* "Energy Transfer in Radiation Processes." Ed. by G. O. Phillips, p. 15. Elsevier, Amsterdam.
8. Phillips, G. O., and Arthur, J. C., Jr. 1964. *Textile Res. Jour.* 34: 497-505; 572-580.
9. Phillips, G. O., Arthur, J. C., Jr., and Hinojosa, O. 1966. *Textile Res. Jour.* 36: 822-827.
10. Phillips, G. O., Barber, P., and Rickards, T. 1964. *Jour. Chem. Soc.* 3443-3450.
11. Phillips, G. O., Worthington, N. W., McKellar, J. F., and Sharpe, R. R. 1969. *Jour. Chem. Soc. A:* 767-773.

HIGH-STRENGTH COTTON KNIT FABRIC WITH DURABLE-PRESS PERFORMANCE AND HIGH LAUNDERING LIFE, PREPARED FROM MERCERIZED YARN [SUMMARY]

by

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(Presented by Alton L. Murphy)

The use of yarn premercerization to improve the DP performance properties of all-cotton jersey knit fabric has been studied, at various levels of dimethylolethyleneurea (DMEU) treatment.

Yarn used in the experimental fabrics was prepared by mercerization, at 1-1/2 percent stretch, of 36/2 gray yarn selected from the same lot as yarn in the control fabrics. Thus the variety of cotton, construction of yarn, and construction of fabric were kept constant in these comparisons. Both the yarn mercerization and fabric knitting were done commercially to ensure complete practicality. The knit fabrics were scoured, bleached, and resin-finished at constant dimensions. DMEU was applied at bath concentrations of 7 to 22 percent (solids), in the presence of polyethylene softener and a commercial zinc nitrate catalyst. Curing was at 300° F. per 4 minutes.

Before DMEU treatment, the unmercerized and the yarn-mercerized fabrics were nearly identical in bursting strength, differing by only 3 to 4 percent. After DP treatment, the yarn-mercerized fabric exceeded by 70 to 75 percent the unmercerized fabric in bursting strength, over the entire range of DMEU concentrations. All of the DMEU-treated yarn-mercerized knits showed extraordinary strength retention. They possessed 93 to 104 percent of the strength of unmercerized, uncrosslinked knit, whereas DP finishing of the latter control fabric decreased its strength to 54 to 61 percent. Actual strength losses in the yarn-mercerized knit fabric were 0 to 5 percent during treatment with 7 to 9 percent DMEU. The losses even at double these resin levels were only 6 to 9 percent.

The efficiency of resin fixation was the same in both yarn-mercerized and unmercerized fabric, as shown by the same nitrogen contents at a given DMEU level, and as also shown by equally high smooth drying and crease sharpness ratings.

In evaluating DP performance, trouser cuffs were prepared of fabric treated with 9 to 18 percent DMEU. These were steam-pressed and then cured. The smoothness ratings were made with AATCC standard replicas and overhead lighting. Smoothness and crease sharpness ratings after five laundering cycles were in the range of 4.3 to 4.8. After 20 to 60 laundering and drying cycles,

smoothness ratings were 3.9 to 4.3, and crease sharpness ratings were 4.2 to 5.0, for test and control cuffs treated with 9 percent DMEU. The ratings imparted by 18 percent DMEU were only slightly higher, and then only in certain instances.

The laundering life of the DP knit cuffs was determined. Not only was the knit construction highly favorable to laundering durability, but also yarn-mercerization increased laundering abrasion resistance at medium levels of DMEU treatment. Unmercerized DP cuffs showed minor damage (thread breakage) after 36 cycles, where yarn-mercerized cuffs required 50 cycles, in fabric treated with 9 percent DMEU. With 18 percent DMEU, 23 to 27 cycles were required for minor damage.

Shrinkage after five launderings was 3.8 to 4.9 percent in yarn-mercerized fabric treated with 9 percent DMEU. In the unmercerized fabric, it was 3.0 to 3.5 percent. However, the presence of 1.35 to 2.70 percent polyvinyl alcohol in the DMEU treating bath, along with 0.9 percent polyethylene, was found to reduce the shrinkage to 1.3 to 1.6 percent (average of wales and courses). The addition of polyurethanes had a similar effect. In the absence of DMEU and polymer additives, the shrinkage was 11 to 12 percent in yarn-mercerized knit fabric, as compared with 10 to 11 percent in the unmercerized knit.

The effect of these shrinkage-controlling additives on laundering abrasion resistance and DP performance of knit cuffs was also determined. Since a polyethylene softener was present, in addition to the polymer additive, the measured stiffness of the fabric was very nearly the same as in the absence of additive. Yarn-mercerized cuffs treated with 5 to 9 percent DMEU, plus 2.7 percent polyvinyl alcohol, withstood 50 to 60 laundering cycles. Unmercerized cuffs treated with 9 percent DMEU plus additive lasted for 36 cycles. Thus, the polyvinyl alcohol, in the presence of softener, had no effect whatever on laundering abrasion resistance.

This additive (2.7 percent polyvinyl alcohol) also had no effect on smoothness and crease sharpness after repeated laundering. After 64 laundering cycles, smoothness ratings were still 4.0 to 4.4 for yarn-mercerized cuffs treated with 5 to 9 percent DMEU

plus additive; crease sharpness ratings were 4.0 to 4.2. The use of 2.7 percent polyvinyl alcohol-4 percent polyurethane did increase these ratings by 0.3 to 0.6 unit, but slightly lowered the laundering life, to 40 to 41 cycles, in the case of yarn-mercerized cuffs.

It is concluded that a unique combination of extraordinarily high strength, laundering life, and shrinkage resistance can be obtained in all-cotton DP knit fabrics, by utilizing yarn mercerization and polymer additive effects.

HYDROPHILICITY IN FLUORO-CHEMICAL STAIN RELEASE POLYMERS [SUMMARY]

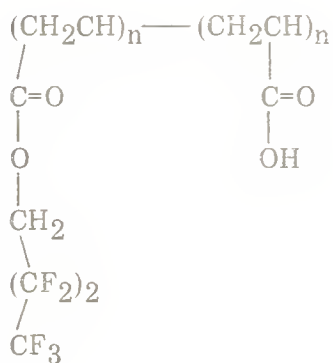
by

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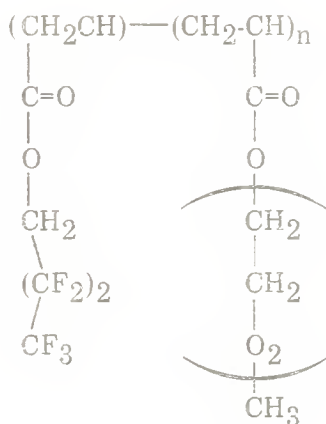
(Presented by J. C. Arthur, Jr.)

The incorporation of hydrophilic moieties in fluorine-containing polymers is recognized as a reasonably efficient means of achieving stain-release and is the basis for one of the commercially available stain-release finishes. Recent publications indicate that this commercial finish incorporates blocks of ethylene oxide units as the hydrophilic portion and a perfluoroalkyl chain attached to an acrylate backbone as the oil-repelling unit. Copolymers of non-fluorine containing acrylates and acrylic acid comprise another class of commercial resins which do not provide oil-stain repellency but can be effective hydrophilic oil-stain releasing agents.

We have recently examined several model polymer systems to compare the carboxylic group and the ethylene oxide unit in fluoropolymer stain-release applications. Two types of polymers, which were employed in this study, are depicted below as copolymers of 1*H*, 1*H*-heptafluorobutyl acrylate and acrylic acid (structure I) and copolymers of 1*H*, 1*H*-heptafluorobutyl acrylate with the acrylate derived from the monomethyl ether of diethylene glycol and acrylic acid (methyl carbitol acrylate), (polymer structure II).



I



II

These copolymers were also compared with their nonfluorinated analogues; that is, where butyl acrylate replaces 1*H*, 1*H*-heptafluorobutyl acrylate in structure I and II. Polymers with structure II will be referred to as ether-acrylate copolymers.

The mole ratios of the two components in each copolymer were varied from 10/1 to 1/3 of nonhydrophilic acrylate, hydrophilic acrylate and the copolymers applied as a 2-percent solution to tri-blend fabrics of wool/cotton/nylon and wool/rayon/polyester. In each case, the tri-blend fabrics had received a pretreatment with a typical formulation used in delayed-cure durable-press finishing. Oily stain release of treated fabrics was measured by a technique patterned after AATCC Test Method 130-1969. Although it was not possible to make direct comparisons between moles of -COOH and moles of -CH₂CH₂O- in the copolymers, several general observations were made.

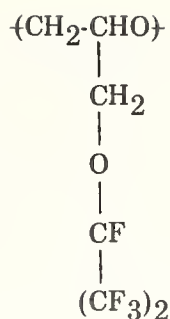
In the acrylic acid-containing copolymers, little or no oil-release properties were observed until the molar concentration of acrylic acid exceeded 50 percent. With molar concentration >50 percent, high oil release ratings were obtained with both fluorinated copolymers and nonfluorinated copolymers; although the fluorine-containing copolymers gave somewhat better results. In the case of the ether-acrylate copolymers, an improvement in oil-release properties was observed which was almost linear with increasing methyl carbitol acrylate concentration. The fluorine-containing acrylates again gave higher release ratings than the nonfluorinated. In terms of overall effectiveness in releasing oil stains, the acrylic acid and ether-acrylate copolymers seemed equally effective at higher concentrations of hydrophilic monomer. In this sense, there would seem little advantage in using one hydrophilic monomer over the other, however, one disadvantage noted with the acrylic acid modified polymers was their increased stiffness. At the levels of acrylic acid found for good oil-release properties the tri-blend fabrics displayed a marked increase in fabric stiffness whereas the ether-acrylate copolymers did not cause an impairment of fabric hand. Two factors seem to account for the improvement in oily stain release for the fluorinated copolymers when compared with analogous nonfluorinated copolymers. The most obvious factor has to do with the smaller quantity of oil actually forced into the fabric during the AATCC staining procedure. The

second factor has to do with migration of the oil stain during aqueous laundering. In cases where the fluorinated acrylates were employed, the oil stains were either completely or partly removed during laundering without a noticeable increase in size of the stained area. However, in cases where the nonfluorinated butyl acrylate was employed, the size of the oil-stained area increased considerably during the laundering process.

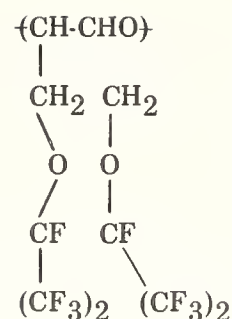
A series of tests were also performed in which the ether-acrylate copolymers were emulsified and coapplied to the fabrics along with the durable-press resin and catalyst. The results of these tests indicated that the fluorine containing copolymers performed almost as well under these conditions as when applied to fabrics as an aftertreatment on durable press type fabrics. However, the nonfluorine containing ether-acrylate copolymers had almost no effect on oil release when coapplied with the durable press formulation. The marked difference in performance of fluorinated vs. nonfluorinated polymers, when coapplied with a durable-press resin, is presumed to reflect the surface-active nature of fluorinated substances which results in a diffusion of these materials to the air/solid interface during high-temperature curing of the durable-press treated fabrics.

A number of different hydrophilic acrylates can be utilized to prepare polymers similar to structure II since a variety of mono-hydroxy polyethylene glycols are available commercially. Some of these were examined and were also found to be effective in oil stain release applications.

In addition, homopolymers were examined in which the ether-oxygen is part of the polymer backbone (structures III and IV).



III



IV

We have reported on polymers from heptafluoroisopropyl glycidyl ether (structure III) previously and noted that, although the polymer does not develop high oil repellency ratings when applied to fabrics, it does exhibit a limited ability to act as an oil stain release agent. Polymer IV, which is derived from 1, 4-bis-(heptafluoroisopropoxy) -2, 3-epoxybutane, develops high oil repellency ratings, however, the polymer does not allow for easy stain removal. We presume then the ether oxygen in this polymer is unable to hydrogen bond with water because of a blocking action from the close-packed heptafluoroisopropyl groups.

CHEMICAL-MECHANICAL COMBINATION TREATMENTS
FOR DURABLE-PRESS COTTONS
[SUMMARY]

by

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and

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(Presented by Glenn P. Morton)

The major criticism of durable-press cotton fabric is its relatively poor abrasion resistance as compared with the original cellulose counterpart. The methods tried in attempts to improve the substandard abrasion resistance of durable-press cotton fabrics are numerous and varied as are the procedures that have at one time or another been used to evaluate this fabric property.

The approaches to improving the abrasion resistance of durable-press cotton fabrics can be generally classified as chemical or mechanical procedures. The chemical methods include additives in the form of fiber-protecting film-formers, or lubricating agents which confer increased fiber mobility. Other chemical methods include selective crosslinking (surface, core, or reactive site) and variations in the molecular structure and reactivity rates of the crosslinking chemical. Mechanical manipulations of the substrate have included alterations in the processing and weaving of yarns. The stretching and compaction of fabrics at different stages of the resin treating process have also been reported. A main objective of the present research was to combine the best features of these different processes into a practical application that would substantially improve the abrasion resistance of durable-press cotton fabrics.

Additives. — A number of chemical additives were evaluated in conjunction with the durable-press treatment for their contributions to the fundamental properties of strength retention, abrasion resistance, dimensional stability, and durable-press appearance. Of the chemical additives tried, a commercial polyurethane was the most effective from an overall standpoint of the products investigated. The group of proprietary products investigated included acrylics, silicones, and various polyolefins.

Polyurethane applications before, in conjunction with, or as an aftertreatment to crosslinking were appreciably beneficial to wrinkle recovery and abrasion resistance properties. Treatment with polyurethane gave a degree of dimensional stabilization even after washing

under extreme conditions. A high temperature cure was necessary to obtain maximum dimensional stabilization. A problem of yellowing is associated with the use of urethanes. When used as a pretreatment, yellowing was not as pronounced as it was when the polyurethane was included in the crosslinking pad bath. The resin used in crosslinking polyurethane-pretreated fabric was found to be most important. For example, cloth crosslinked with dimethylol methyl carbamate had three times the resistance to laundry abrasion as the fabric treated with dimethylol propyleneurea.

Mechanical stretching. — Various studies were designed whereby the effects of stretching in conjunction with fabric crosslinking could be determined. Fabric stretching was performed on raveled strips in the untreated condition, as pretreatment to resin treating, and as an integral part of the crosslinking process. Similar methods were applied to swatch size and full width cloth.

The tensile strength of cotton cloth was increased by a stretching process which in turn reduced elongation-at-break. Stretching of raveled strips as an integral part of the crosslinking process gave increases in tensile strength, but concomitant losses in wrinkle recovery practically nullified this approach to improve durable-press cotton. A pretreating process in which fabric was stretched and stabilized in the stretched condition by polyurethane treatment made possible a crosslinked fabric with improved tensile strength, and desirable wrinkle recovery. The stretching process appeared to reduce warp flex abrasion resistance, but had little effect on the filling. Slack mercerized cloth treated in this manner had better physical properties than unmercerized cloth. Slack mercerization imparted a high degree of shrinkage; thus, it was possible to achieve higher tensile strength values by stretching the shrunken fabric back to its original dimension before crosslinking.

A specially designed frame was utilized to stretch swatches of cloth. This made it possible to evaluate not only the stretched specimen, but also samples taken from

the resulting shrunken dimension of the swatch. The stretched specimen appeared to gain in tensile strength, while those samples taken from the shrunken dimension benefited in abrasion resistance.

Compaction. — Some of the investigations of fabric stretching indicated that the stretched dimension gained in tensile strength while the resulting compacted, or shrunken direction increased in abrasion resistance. Because this increase in abrasion resistance might be related to the elongation or crimp imparted to the treated cloth, this possibility was investigated. Both cotton broadcloth and twill fabrics were compacted in the warp direction by compressive shrinkage (Sanforization). The complete treatment entailed padding the cloth with polyurethane, drying at bleached dimension, Sanforizing, curing the polyurethane, and crosslinking.

This type of pretreatment more than tripled the Stoll flex abrasion resistance of the resin-treated broadcloth. The abrasion resistance of the twill cloth was also improved by this combination of treatments, but not to the same degree as the broadcloth.

Pilot plant trials. — Various combinations of the chemical and mechanical treatments that showed indications of improving the abrasion resistance of crosslinked cotton were applied on a full width scale to 8-ounce cotton twill. The combination of filling stretching of polyurethane-impregnated cloth before crosslinking with a process that included Sanforization at the "sensitized" stage gave 30-percent higher tensile strength and a 50-percent increase in laundering durability than was obtained by a single pad-dry-cure process.

Slack mercerization was utilized as a pretreating process to impart greater crimp in the warp yarns of subsequently crosslinked cotton twill fabric. This pretreatment combined with further warp compaction of the "sensitized" fabric gave 20-percent added tensile strength, 25-percent increase in tearing strength, and 50-percent increase in the wear life of laundered cuffs over that obtained from conventionally crosslinked samples.

THE EFFECT OF FORMALDEHYDE CROSSLINKING OF COTTON ON THE CHAIN LENGTH OF THE CELLULOSE MOLECULE. I. THE FORM W'PROCESS [SUMMARY]

by

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(Presented by Leon Segal)

Crease resistance or durable-press properties bestowed on cotton fabrics by the customary processes which crosslink cellulose are accompanied by losses in tensile strength, abrasion resistance, and the like. For many years such losses were attributed to factors induced only by the crosslinking of the cellulose molecules, as for example, improper distribution of strain among the fiber elements during stressing. Much study has been given to many of the parameters involved, and many conclusions have been drawn from these studies. However, only little consideration has been given to the chemical aspects insofar as they relate to effects on the cellulose molecule itself which is being reacted with the crosslinking agents.

In 1960 Frick, Andrews, and Reid looked at the physical properties of cotton fabric treated with dimethylol urea, with dimethylol ethyleneurea, and with formaldehyde, where zinc nitrate was used as the catalyst. They found that the catalyst control fabrics had lower breaking and tear strengths than the untreated fabric, and that the losses were greatest for the catalyst control for the formaldehyde series. A simple measurement of the degree of polymerization (DP) of these controls revealed changes in this parameter, this being most marked for the formaldehyde control. These workers concluded that variations in tear and breaking strengths at equal crease recovery angles are explainable by differences in cellulose degradation caused by the acidic catalyst.

In the following year, however, Steiger and coworkers concluded that the poor crease recovery — strength relationship exhibited by cotton reacted with formaldehyde does not arise from the degradative effects of acid, but is a function of the formal linkage. In other words, the loss of strength is an essential element rather than an undesirable byproduct of the crease-recovery process.

In a later work, Joarder, Brannan, Rowland, and Guthrie found that small decreases in DP and tear and breaking strengths of fabric heated to 125° C. in a closed system were more pronounced when boric acid was present in the system. When retention of tear and breaking strengths of the formaldehyde-modified fabrics were considered as a function of treatment time, the products of the catalyzed reaction displayed greater losses.

It is highly significant that so many of the conclusions regarding strength loss of formaldehyde crosslinked cotton fabrics are based not on changes in DP of the cellulose backbone but rather on the results of textile tests made on the treated fabric. Yet it is well known beyond question that the tensile strength of a polymer is a function of its DP. The lack of necessary DP data in prior work is understandable in that these crosslinked cottons are insoluble in the solvents used for measurements of DP. Nevertheless, surmounting of this obstacle became possible in 1967. Lewin and Weinstein found that the nitration method for the determination of DP was applicable to cottons crosslinked with formaldehyde. By this means they were able to show that the tear strength of a treated fabric decreased as its DP decreased, there being a straight-line relationship between tear strength and the reciprocal of DP for cottons containing up to 0.9 percent formaldehyde.

Following this lead, then, a cotton fabric treated by the Form W' process (16 percent formaldehyde, 14.6 percent HCl, 69.4 percent water; reacted at room temperature) over a period of time up to a level of 1 percent formaldehyde was nitrated for study of changes in DP and in DP distribution. Data in these areas were obtained by viscometry and gel permeation chromatography (GPC). The results were related to several tensile parameters.

All test data on these samples — breaking strength, elongation at break, tear strength, and flex abrasion — decreased in the same manner with the time of treatment, as did the viscometric and GPC data, but without a regular trend until plotted against the reciprocal of DP. With this, then, a very rapid linear decrease in tensile properties for samples treated up to 60 minutes was observed, after which the rate of loss slowed very markedly. It was at about this point, too, that the wet and dry wrinkle recovery angles began to level out.

Gel permeation chromatography showed immediate shifts in DP to shorter chain lengths with treatment time as low as 1 minute. This shift was very pronounced after 6 hours, indicating a high degree of degradation. The breadth of the chromatograms progressively broadened with treatment time, this effect being the result of the buildup of lower DP cellulose.

When one considers that the treating solution for the Form W' process is 14.6 percent in hydrochloric acid, the acidic catalyst, then the degradation observed is easily explained. These results also strongly support the earlier conclusions of Frick and coworkers. Because there are two competitive reactions proceeding simultaneously

during the treatment — chain cleavage and crosslinking — further studies are needed on variations in the treatment of cottons with formaldehyde and other crosslinking, wrinkle-resistant finishes to procure the necessary data that can lead to improved performance in the end-use product.

METHODS FOR REDUCTION OF FREE FORMALDEHYDE IN CARBAMATE-SENSITIZED FABRICS [SUMMARY]

by

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In the post-cure process for producing durable-press garments and household items, fabrics are impregnated with a formaldehyde-amide adduct agent and dried at the finishing plant. Conditions of drying are such that there is essentially no reaction between the agent and the cellulose substrate of the textile material. The sensitized fabric, as it is called at this stage of the process, is packaged, warehoused, and eventually shipped to the garment cutting plant for final processing. The sensitized fabric is cut, sewn, and trimmed, and then pressed to shape and cured by oven treatment. The latter brings about reaction between cotton and the agent which crosslinks the cellulose molecules to make the pressed shape durable to repeated launderings and wearings.

The release of free formaldehyde during cutting and sewing operations has been a problem which has restricted the use of certain finishing agents in the post-cure process. Methylolated carbamate agents have been criticized frequently as being particularly offensive for formaldehyde release. Their utilization in post-cure durable-press finishing has been limited, but it has been suggested that reduction of formaldehyde release from carbamate-sensitized fabric could increase usage of these agents substantially. Because a cotton-containing textile finished with carbamates has well known desirable characteristics, remedies have been sought for the problem of formaldehyde release.

Free formaldehyde is not bound nor held chemically in the fabric. It thus can volatilize and provide a source of irritation to workers who must handle the sensitized fabric. The phenomenon may be considered a type of industrial air pollution and health hazard. This formaldehyde comes from two sources: 1) free formaldehyde in the pad bath, that is deposited in the cloth during impregnation and remains after the drying (sensitizing) treatment; and 2) formaldehyde released by dissociation of the methylolated carbamate agent in the sensitized cloth.

In the authors' previous work, reported at the Cotton Utilization Research Conference last year, it was found that physical removal of free formaldehyde from

concentrated solutions of dimethylol carbamates was not practical. However, it was possible to chemically bind the free formaldehyde by treatment of carbamate solutions with a suitable reactant such as ethyleneurea or sodium sulfite. Although these modifications were effective in reducing the amount of free formaldehyde in the carbamate solution, and consequently in the sensitized fabric, there also were some undesirable collateral effects on the properties of the finished fabric. Furthermore, these modifications entailed additional costs for chemicals and chemical processing.

In the present work, another approach to the problem has been taken. Research effort has been directed toward removal of free formaldehyde from the sensitized fabric without costly chemical treatments or the need of elaborate equipment and processing. In addition, processing factors have been identified which influence the magnitude of the amount of free formaldehyde in cotton sensitized by treatment with dimethylol methyl carbamate. Release of formaldehyde by dissociation (decomposition) of the methylolated carbamate in sensitized fabric also has been monitored. Changes in chemical analyses of the fabrics upon storage with free access to the atmosphere and in sealed plastic bags were determined. Various carbamate agents and other commonly used durable-press finishing agents were compared.

Techniques have been developed in which free formaldehyde can be eliminated from sensitized fabrics without adverse effect on handling the fabrics in the established post-cure process or on the properties of the resulting durable-press products. The free formaldehyde is released from the fabric and carried away by aeration with moist air or by steaming. Various methods of aeration and steaming have been investigated, and conditions established for reducing the amount of free formaldehyde in the fabric to acceptable levels. Free formaldehyde content has been determined quantitatively by the sodium sulfite titration procedure and qualitatively by observation of the odor. The AATCC sealed jar test method also has been used to verify decreased formaldehyde release from processed fabrics.

In addition to the theoretical value of the findings of this research, the practical worth has been demonstrated in a semipilot-plant experiment in which the free formaldehyde was released from carbamate-sensitized cotton print cloth by steaming in a flash ager. Adaptation to plant procedures of these methods for removal of free formaldehyde could spur greater use of carbamate agents, with their attendant advantages, in post-cure durable-press finishing. By using the techniques described, the finisher

should be able to package a sensitized fabric with no free formaldehyde. Alternatively, removal of the free formaldehyde could be accomplished by adding a simple processing step at the garment cutting plant. Although these processes for removal of free formaldehyde were worked out on carbamate-sensitized cotton, they should be applicable also to fabrics treated with other methylol amide agents.

DECRYSTALLIZATION OF COTTON CELLULOSE YARNS BY DUAL-TREATMENTS WITH QUATERNARY AMMONIUM HYDROXIDES AND ALKALI METAL HYDROXIDES [SUMMARY]

by

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(Presented by Tyrone L. Vigo)

Kiered 12/3 cotton yarns undergo extensive, but temporary, decrystallization when wet in the slack state with 2.1 *N* (33.5 percent w/w) aqueous benzyl-trimethylammonium hydroxide. Washing and air-drying cause the yarn to recrystallize to Cellulose I. However, much of the decrystallization can be rendered permanent, if the quaternary ammonium hydroxide-wet yarns are centrifuged, then immersed in aqueous solutions of sodium or potassium hydroxide before washing and air-drying. This aftertreatment also produces greater shrinkage and elongation than either alkaline treatment alone.

Of the three alkali metal hydroxides used, sodium hydroxide was the most effective. Aftertreatments employing concentrations of 1, 5, or 13 percent sodium hydroxide showed little, if any, difference compared with the quaternary ammonium hydroxide alone with respect to reduction in crystallinity and conversion to Cellulose II. However, 18 or 23 percent NaOH as aftertreatments reduced the X-ray crystallinity (calculated as crystalline order) to values of 0.35. It also caused extensive lattice conversion (measured as the intensity ratio $10\bar{1}/002$) to give values of 0.86 and 0.95, respectively. Native cotton has a crystalline order of 0.80 and a $10\bar{1}/002$ ratio of 0.18, while cotton treated with 23 percent NaOH had a value of 0.56 for crystalline order and of 0.95 for the lattice conversion ($10\bar{1}/002$) ratio. The percent shrinkage for these two yarns was 56 percent compared with 21 percent for the NaOH alone, or compared with 33 percent for 2.1*N* aq. benzyltrimethylammonium hydroxide (BTMOH) alone.

Aqueous solutions of potassium hydroxide (KOH) were almost as effective as those of sodium hydroxide in causing decrystallization and lattice conversion. The use of 1, 5, or 10 percent KOH as an aftertreatment produced little effect with respect to these two parameters; however, 20 and 32 percent KOH solutions produced a marked reduction in crystalline order (values of 0.52 and 0.42, respectively) and substantial conversion to Cellulose II ($10\bar{1}/002$ values of 0.76 and 0.87, respectively) occurred. Percent shrinkage was 48 and 56 percent, respectively, on these yarns receiving this dual treatment.

In contrast to sodium and potassium hydroxide, lithium hydroxide (LiOH) solutions used as an aftertreatment showed hardly any difference from the effect of the BTMOH alone. This was true with concentrations of 1 and 5 percent LiOH, as well as with 9.5 percent LiOH (the maximum swelling concentration of this particular alkali metal hydroxide with cellulose).

The effect of tension applied during various stages of these dual treatments was also investigated with respect to lattice conversion to Cellulose II, orientation, and crystalline order. As previously noted, 2.1 *N* aq. BTMOH treated yarn, when washed with water, gives Cellulose I. This is true whether it is treated slack (S), at constant length (NL), quaternary hydroxide-wet yarn is immersed slack into 23 percent NaOH, then water washed and dried, substantial conversion to Cellulose II occurs; this cannot be greatly reversed even when the water washed yarn is restretched to 70 percent NL before air-drying. Lattice conversion still occurs to a large extent in yarns treated at NL (with BTMOH), then at NL with 23 percent NaOH (value of $10\bar{1}/002$ ratio = 0.77). This is also true for yarns treated S, NL (with BTMOH), then at NL with 23 percent NaOH (ratio was 0.57). Evidently, the added tension in latter treatment prevents full conversion to cellulose II.

These treatments mentioned above have similar effects on crystalline order. Yarns treated slack with 2.1 *N* aq. BTMOH, then with 23 percent NaOH, undergo marked reduction in crystallinity, which cannot be reversed by restretching the yarn after it is water-washed. However, yarns given a double NL treatment with BTMOH and 23 percent NaOH have higher crystallinity (value of 0.55) than do those treated S, NL with BTMOH, then NL with 23 percent NaOH (0.65). It can be seen, therefore, that tension does effect these parameters. Orientation is also affected by tension in these dual treatments. The dual slack treatment of yarn with 2.1*N* aq. BTMOH and 23 percent NaOH produces only a slight increase in orientation over that of untreated cotton (the 50 percent X-ray angle decreases from 30.0 to 26.3). However, a dual NL treatment increases the orientation, the X-ray angle being 17.8 compared with 24.8 for one NL treatment with BTMOH alone. Similarly,

treatment at S, NL with BTMOH, then NL with 23 percent NaOH increases the orientation to give a 50 percent X-ray angle of 16.0. However, this treatment is not as effective as that of S, NL with BTMOH alone (value of 14.6).

The effect of tension on the breaking strength before and after crosslinking with 7 percent DMEU was also noted with these dual treatments. During crosslinking, samples treated with a dual slack treatment of BTMOH and 23 percent NaOH retained only 25 percent of their strength, while those treated with a dual NL treatment retained 72 percent of their strength. Their strength even after crosslinking equalled or exceeded that of untreated

cotton. The S, NL treatment with BTMOH, followed by NL treatment with 23 percent NaOH, was no more effective than the dual NL treatment (70-percent strength retention, overall strength comparable with native cotton). Treatments involving BTMOH alone at NL or S, NL were not nearly as effective in showing strength retention after crosslinking. The dual NL treatment is superior also to that of a NL treatment with 23 percent NaOH alone, particularly in terms of absolute strength (5.5 pounds for the former, and 4.8 pounds for the latter). A high degree of lattice conversion, high orientation, and a moderate degree of crystalline order are thought to contribute to the desirable physical properties of the sample having a dual NL treatment.

MINERAL DYEING PROCESS FOR COTTON TO IMPART MILDEW AND WEATHER RESISTANCE [SUMMARY]

by

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(Presented by Hubert H. St. Mard)

A general method of pearl gray mineral dyeing is to impregnate the fabric with chromic chloride, iron sulfate or chloride and dry to about 7 to 8 percent moisture content. The fabric is then padded through a caustic-soda ash solution to fix the color; washed and dried.

A critical part of the process is the first drying step. Overdrying causes fabric tendering due to the free acid of the mineral bath. Underdrying causes surface and external pigment formation.

An analysis of the problem indicated that this acid damage could be minimized by the use of organic buffers such as urea and other nitrogen containing compounds.

The fabric was a scoured and bleached 8 oz. lined duck. The samples were padded through a 5 percent chromic chloride bath to a wet pickup of about 50 percent, and then dried at different time intervals to determine the amount of strength loss. A drying temperature of 282° F. was arbitrarily selected, as this is within the range of commercial applications. There was a gradual strength loss on continued drying and after five minutes there was only 65 percent retention.

This experiment was repeated using varying amounts of urea as an acid acceptor. Increasing the urea content resulted in an increase in strength retention. With only about 10 percent urea added, the fabric showed practically no strength loss.

Methylolmelamine type resins were tried as buffers. It was anticipated that both the rot and weather resistance of the fabrics could be improved. The chromic chloride was also expected to act as the acidic catalyst for resin fixation. The samples prepared with the highest amounts of resin had the best initial breaking strength and also highest resistance in the soil burial beds.

A set of samples was run using urea with the resin. The use of urea alone caused no increase in rot resistance as compared with the chromic chloride treated control. The samples with the best initial breaking strength were those containing both urea and resin, although these samples had the lowest soil burial resistance. It is apparent that urea inhibits soil burial resistance.

Included in the above experiment were a methylolmelamine and a methylated methylolmelamine resin. The methylated resin-treated sample had considerably better soil burial resistance. Using 10 percent resin and 10 percent urea in the chromic chloride formulation, fabrics were produced with initial strength retentions in excess of 90 percent. The rot resistance would be considered sufficient for outdoor weather exposure as the sample lasted for the entire six weeks soil burial period.

Urea formaldehyde resin was used as buffer with and without added urea. The results were similar to the use of the melamine resins. The best samples for soil burial resistance were those containing no urea as these samples retained practically all initial strength in the rot burial test. The samples with urea exhibited the higher initial strength retention and also lasted through the soil burial exposure with some strength loss.

Urea and formalin in varying ratios were used in the padding formulation so as to form urea formaldehyde resin in situ. These samples also had very good rot resistance lasting through the entire 6-weeks test. These results indicate that this type of resin treatment could be substituted for the melamine resins.

A complete weathering study is being made of all the urea- and resin-treated samples. At this 9-month stage, the samples treated with chromic chloride without additive buffers have only about 40 percent strength retention. This is in the same range as the untreated control. The samples with urea alone as buffer have retained about 50 percent of their original treated strength. The fabrics treated with equal amounts of resin and urea in the mineral dye formulation have the best weather resistance. Those samples containing urea have slightly higher values than those with resin alone. Both the melamine and methylated melamine samples have the same strength values.

Ferric chloride alone and in varying ratios with chromic chloride were used. These gave colors ranging from green to tan. Using ferric chloride alone and with no buffer produced fabric with very low strength due to the very high acidity of this salt. When about 10 percent urea

was used with it, the fabric had no initial strength loss. The ratios of the two salts can be varied in either direction with no resultant strength loss when urea is used.

An added advantage of using the resins is their pigment binding capacity. A study is planned using various metal salts for producing different colored fabrics. These salts can be used to cause resinification and the resin polymers formed will lock in the pigment and mineral colors.

UTILIZATION OF DISCOUNT COTTON IN YARN MANUFACTURING [SUMMARY]

by

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(Presented by Harry E. Arthur)

In the years 1960 to 1968 the Commodity Credit Corporation of the U.S. Department of Agriculture accumulated large stocks of low micronaire, off-white cottons (3.0 and below) in the 1-inch and shorter staples, along with a lesser amount of high micronaire, short staples (5.0 and above). Considerable amount of concern was expressed by various segments of the cotton industry over the ultimate consumption of this "discount cotton." The Southern Utilization Research and Development Division of the U.S. Department of Agriculture in order to stimulate the use of this cotton, entered into contract with the Textile Research Center to determine the spinning potential of blends composed of these cottons. During the period of this program, the CCC stocks were depleted to a very low level. However, weather and environmental conditions, economics, and whims of cotton producers and buyers can easily produce another surplus of these cotton types, and utilization may again be a problem.

Textile mills are blend oriented, thanks to man's ingenuity in producing fibers and creating uses for them in combination with the natural fibers. Most spinning and fabric structure mills have experienced the problems associated with mixing fibers of varying lengths, diameters, and stress-strain characteristics. The acceptance of these combinations is universal, ironically, except when applied to all-cotton mixes. It would be unheard of to blend two cottons with 1/4" staple difference, but with a synthetic/cotton blend it is commonplace. It would be an unusual mill operation to blend two cottons differing by 25,000 p.s.i., but not in blending synthetic fiber with cotton with these comparable differences. Other comparisons can be made, such as blending synthetic costing 60 cents per pound with cotton costing 32 cents per pound, but not blending two cottons that differ in price as much as 10 cents per pound.

The research being reported in this paper is unique because two Micronaire cottons, 5.5 and 2.7, were blended together. The procedures followed to insure uniform fiber blending did not vary from conventional methods for processing cotton with synthetic fiber. Conventional equipment was used and mill-scale tests were made.

Two staple lengths were used: 15/16 inch and 1 inch. Three grade combinations within each staple constituted the second screening. Grade blend one was composed of 50 percent Strict Low Middling White and 50 percent Strict Low Middling Light Spot. Grade blend two constituted a combination of 50 percent Strict Low Middling White, 25 percent Low Middling Light Spot, and 25 percent Low Middling Spot. Grade blend three included 50 percent Middling White, 25 percent Middling Light Spot, and 25 percent Middling Spot.

Within these grades and staples, the following Micronaire combinations were blended to obtain a 3.8 Micronaire — the same as the control cotton: 5.0 with 3.1 (MHML), 5.5 with 2.7 (EHEL), and approximately 50 percent 3.8 with 5.3 with 3.0 (HML).

Two blending methods were used: hopper weigh-pans and breaker drawing sliver. The control cottons (within each grade blend) and the HML blend were processed through the weigh-pans only; and the other blends, MHML and EHEL, were processed through both weigh-pans and the drawing, as far as blending techniques are concerned. Two complete studies, or two replications, on each blending combination were made.

Preliminary studies included carding rates for all of the different Micronaire levels. These studies included small scale spinning tests. Results of these tests made it possible to settle on 27 pounds per hour card production for the hopper blends and the control cottons, 10 pounds per hour on the low Micronaire cottons that were to be blended on the breaker drawing frame and 44 pounds per hour for the high and extra high Micronaire cottons for the drawing blends.

Tests that were made on stock in process and the finished yarn included fiber tests on the individual bale samples, picker laps, card web, and finisher drawing sliver; opening, picking, and carding waste percent; neps; ends down per thousand spinning hours; yarn skein strength and appearance; yarn single strand strength, elongation, coefficient of variation, neps per 1,000 yards, and irregularity coefficient of variation.

Results of these tests indicate that, in many cases, the hopper blends produced yarns equal to or better than the control cottons and, in a lesser number, so did the drawing blends.

CONCLUSIONS AND RECOMMENDATIONS

The study showed little or no significant differences between grades. A logical choice therefore, would be for industry to use the cheapest grade combination which is Grade II — 50 percent Strict Low Middling White, 25 percent Low Middling Light Spot, and 25 percent Low Middling Spot. This combination is presently 235 points cheaper than Grade III.

The entire study lacked any consistent pattern wherein one blend of Micronaires was better or worse than others. This in itself indicates that the various combinations of Micronaire blending are feasible and compare favorably with the control cottons. Again, the recommendation would be to blend the extremes of Micronaire in the discount range in controlled proportions to achieve an average Micronaire of 3.8 to 4.2, thereby saving the most money.

The drawing frame blends were more expensive to produce. Since the results show that these blends were no better than weigh-pan blends, our recommendation is to use the latter.

Blends of cottons of different Micronaire and grade are not only possible, but highly practical when modern blending techniques are followed. The hopper weigh-pan method is the least costly, from a labor point of view. Indications, particularly in the longer staples, are that the hopper weigh-pan method produces the best yarn.

This research has shown that discount cottons with a range of fiber properties can be blended successfully, provided care is exercised in controlling the percentages of the components. It is essential, however, that the physical properties, color, and nonlint content of the individual bales be known and the blend components be held as consistent as possible.

A continuation study based on the above results is being made at present. The yarns produced from Grade II, EHEL, 1" staple will be made into nine constructions of fabrics for further evaluation.

THE DURABLE PRESS PERFORMANCE OF FABRICS PREPARED FROM BLENDS OF COTTON AND RESIN SENSITIZED COTTON

by

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ABSTRACT

A series of cotton durable press fabrics was prepared from a 50/50 blend of cotton and cotton containing uncrosslinked durable press resin. The fabrics, totaling 101 in all, were prepared from eight different yarns and include three weave variations in two weight classifications (nominally 5.4 and 8.1 ounce per square yard). Samples of each of these fabrics have been evaluated. It has been possible to determine the influence of yarn construction, fabric geometry, and weave upon the dimensional stability and durable press properties of these fabrics. Lighter weight highly interlaced fabrics were more dimensionally stable than open weave heavier weight fabrics. Abrasion resistance on the other hand required fabric constructions which are, in many instances, contrary to those required to achieve fabric dimensional stability. Abrasion resistance has not been found to be dependent upon fabric weight. Low cover factor 3 x 2 twill weaves were more abrasion resistant than high cover factor 3 x 1 or plain weave fabrics. Optimization of dimensional stability and abrasion resistance characteristics could be achieved by using a two-ply warp and very fine filling yarns.

INTRODUCTION

Preliminary research at the Southern Utilization Research and Development Division of USDA has shown that blends of resin treated and untreated cotton fibers will produce fabrics for durable press all cotton apparel having up to eight times the abrasion resistance of apparel made from conventionally resin-treated cotton fabrics. The major problem handicapping this development is the excess laundering shrinkage of apparel produced from fabrics made from such blends of fibers. This shrinkage is reported to be as high as 5 percent in the warp and 2 percent in the filling direction. Ideally, from the consumer's point of view, shrinkage, as evaluated by the AATCC wash and tumble dry test, should be 1 percent or less. The objective of this investigation was to develop fabric constructions for improving the dimensional stability of abrasion resistant durable press fabrics prepared from a 50:50 blend of resin treated and untreated cotton fiber.

FIBER, YARN AND FABRIC PROCESSING

In performing this investigation, it was necessary to devise a semi-commercial procedure for sensitizing part of the cotton for the preparation of the cotton blend and its subsequent conversion into fabric.

All the fabrics constructed and studied were prepared from a blend of 50 percent by weight of long staple cotton fiber and 50 percent of the same fiber which has been sensitized with Permafresh 183. This blend was made up of equal parts of middling grade Carolina Queen, Delta Pine and Acala cottons, and represented 3 geographical areas. Fiber quality was selected suitable for the spinning of singles yarns to a fineness not to exceed 44's cotton count.

The lots of cotton employed were blended, opened, and cleaned following standard mill practice, scoured and bleached, and half of the fiber set aside. The remaining half was dyed blue and resin treated in stock form to 11 percent pick up of unreacted resin. The first batch of resin-treated fiber was processed on a wool scouring train, replacing the wash liquor with the resin solution. The resinated fiber was then extracted and dried at low temperature to 20-percent-moisture content. A second batch of resinated fiber was processed in a kier, and this has proved to be a more efficient process.

Six singles yarns were prepared to include three yarn counts, namely, 44/1, 22/1, and 11/1 (for example, 13.4, 26.8, and 53.7 tex) at twist multipliers of 3.5 and 4.5. Using 44/1 yarns of similar twist multiplier, two 44/2 plied yarns were constructed, both plied to balance at 28S. Similarly, using 22/1 yarns of similar twist multiplier, two 22/2 plied yarns were constructed plied 16.5S to balance.

The plied yarns were used for the warps of the fabrics constructed. In selected instances, plied yarns have been used as filling. Singles warp yarns could not be justified because the conventional warp sizes required with singles warp yarns interfere with the uncured resin present in 50 percent of the fiber blend.

These eight yarns were used to construct 101 fabrics, using two ply size free warps. Three weave geometries (plain, 3/1 and 3/2 twill) and two weight categories (5.4 and 3.1 ounce per square yard) were employed. Within each weight category, cover factors, yarn count, twist multipliers and crimp geometry were varied according to a predetermined plan with a view to identifying the influence of constructional variations upon dimensional stability, fabric and weave structure. It was intended to establish fabric engineering and construction principles to permit the manufacture of durable press fabrics with the greatest prospects of achieving dimensional stability and at the same time maintaining other desirable or necessary fabric properties. While it was intended to achieve most of this dimensional stability by correct yarn, fabric and weave structure, it is to be expected that the final attainment of acceptable dimensional stability in both 5 and 8 ounce fabric weights will require mechanical and/or chemical finishing procedures. Consequently, design parameters distilled from this investigation will be used to construct fabrics which will also be responsive to suitable finishing operations. Subsequent phases of this investigation will consider mechanical and chemical finishing as a means to achieve dimensional stability and acceptable durable press performance.

FABRIC TESTING AND EVALUATION

Each of the fabrics produced was subjected to a series of tests and evaluations to determine dimensional stability and simulated garment and consumer-use performance both in the flat-cured state and also as a pants cuff assembly. This evaluation has involved performing the following tests and determinations using, wherever possible, standardized ASTM and/or AATCC procedures.

Yarn Count, Ends and Picks (ASTM-D1910-64)

Fabric Weight (ASTM-D1910-64)

Tensile Strength Measurements (ASTM-D-1682-64)
Cut Strip Method

Planar Dimensional Stability (ASTM-D-1905-61T)
after 1, 10, 20, 40, and 80 Laundering Cycles

EVALUATION OF CUFFS

Cured fabric abrasion resistance and dimensional stability measurements were made on short trouser cuff assemblies, essentially the last 12 inches of a cuffed trouser leg. The purpose of this testing was to evaluate the abrasion resistance of the cuff, particularly the cuff points, during laundering and tumble drying. Dimensional stability measurements were also made, intended to corroborate planar shrinkage determinations which were performed upon cured flat fabric squares.

FABRIC PRESSING AND CURING PROCEDURES

Samples of flat fabric to be used for cuffs, dimensional stability determinations, and physical testing were subjected to the same pressing procedures before curing to insure that the heat and steam history of all test materials was identical.

Pressed cuffs and flat fabric samples were cured in a horizontal air flow oven operated with partial air recirculation with the exhaust half opened at a curing temperature of 320° F. (160° C.). Samples were mounted with the warp yarns hanging vertically and the specimens held parallel to the air flow direction. Each rack of fabric samples was exposed in the oven, at 320° F. for 8 minutes to effect a cure of the resin in the fabric. The racks were removed and allowed to cool. The cuffs were removed from the racks and stacked in anticipation of subsequent experimentation.

LAUNDERING AND DRYING

Cured planar shrinkage samples and cured trouser cuffs were subjected to repeated laundering and drying using automatic washers and electric dryers. Both sets of washers and dryers used were checked to insure that sequence times, temperatures, and general functions were identical. A normal wash cycle was used lasting 10 minutes and each wash load weighed 4 pounds. The total washing cycle took 28 minutes to complete.

TEST DATA AND RESULTS

Fabric shrinkage was experienced during pressing and curing. While not all the fabrics shrank equally, as much as 3-percent-warp direction shrinkage could occur, which represented approximately one-third of the total warp direction shrinkage noted after 80 launderings. Filling direction shrinkage resulting from pressing and curing usually did not exceed a half a percent, and in some instances grew rather than shrank. About half of the potential warp direction shrinkage was experienced during the first laundering cycle and was complete by the fortieth laundering cycle.

Dimensional stability was influenced by fabric weight. We found that the 5.4 ounce fabrics had better dimensional stability than the 8.1 ounce fabrics. The degree of improvement depended upon the weave pattern with the plain weaves evidencing the best dimensional stability properties. The 3 x 2 twills were not as dimensionally stable as the plain weave fabrics but were better than the 3 x 1 twill fabrics. Increasing warp or filling cover factors or both played a significant roll in improving fabric dimensional stability. Decreasing the fabric weight from 8.1 to 5.4 ounces could reduce the warp direction shrinkage by as much as 4 percent. On the

other hand, changing the weave pattern from plain to 3/2 twill or 3/1 twill could increase warp direction shrinkage by 0.5 to 2 percent for the 5.4 oz fabrics, and by 1 to 3 percent for the 8.1 oz fabrics.

Yarn construction played a less dramatic but, nevertheless, significant role in controlling dimensional stability. As might be expected the lower the warp twist multiplier the better the fabric dimensional stability. Reduction of the warp singles yarn twist multiplier from 4.25 to 3.5 could reduce warp direction shrinkage by as much as 3 percent. However, changes in filling twist multiplier did not significantly influence either warp or filling shrinkage. Changes in filling yarn construction did influence dimensional stability, with singles filling yarns able to maintain better fabric dimensional stability than plied yarns. Using singles filling rather than ply filling could reduce filling direction shrinkage by approximately 0.5 percent. Also, it was noted that the reduction of filling yarn size and the use of large number of fine filling yarns at constant fabric weight would lead to better fabric dimensional stability. The minimum warp shrinkage apparently attainable in these fabrics after 40 launderings is 2.5 percent, based upon the loom state fabric dimensions (1.6 percent based upon cured fabric dimensions).

CUFF ABRASION RESISTANCE, APPEARANCE RETENTION, AND DIMENSIONAL STABILITY

Cuffs were examined in detail after 1, 10, 20, 40, and 80 washings/laundryings. Cuff dimensional changes were noted, abrasion ratings made, and the nature of the abrasive damage quantified. Each abrasion rating was made on the basis of the number of holes falling within a specified size classification, multiplied by a factor.

Cuff appearance and crease retention characteristics were assessed after 1, 10, 20, 40, and 80 laundering cycles using techniques described by Goldstein and May and AATCC Standard 88A, 88B, and 88C — 1964T.

CUFF ABRASION RATING

Cuff abrasion was analyzed as a function of fabric weight and weave. We found no clear-cut statistical influence of fabric weight upon abrasion resistance. Changes in fabric cover factor, which can cause changes in fabric weight for the same weave, end or pick count, were shown to influence abrasion resistance. In fact, a reduction in fabric cover factor by the reduction of either end or pick count yielded the most abrasive resistant fabrics. A high fabric cover factor in any of the weave types studied was synonymous with poor abrasion resistance. Examination of the weave types revealed that the 3 x 2 twill weaves possessed the best abrasion resistance (surviving 80 washes) somewhat better than the 3 x 1 twill fabrics (severely damaged at 40 washes) and

considerably better than the plain weave fabrics, where many abraded quite rapidly and could not survive 40 laundryings. At the yarn level, it was determined that for the range of warp and fill twist multipliers studied, there was no apparent influence upon cuff abrasion resistance. The use of ply filling yarns, as opposed to singles filling yarns, did result in a significant improvement in fabric durability.

The dimensional stability of the pants cuff assemblies correlated perfectly with the planar shrinkage data and hence the same conclusions apply. Cuff appearance and crease retention ratings were consistently good.

At the 40 wash level, it was unusual to find cuffs with either appearance or crease ratings less than 3.5. Crease ratings of less than 3.5 after 40 washes, and after 80 washes were attributable to loss of fiber at the crease, with the crease behaving as a low friction hinge, rather than a fixed crease.

SUMMARY

To summarize the test data obtained for fabrics it is necessary to qualify the primary yardstick, that is, dimensional stability, with an appreciation of fabric durability. The dichotomy is quite apparent in that one can design structures with excellent dimensional stability but which are impossible to weave according to industry criteria and which have extremely poor abrasion resistance. On the other hand, one can cite constructions with superior abrasion resistance but exceedingly high planar cuff shrinkage. Faced with these ineluctable inverse correlations, one must compromise. The optimum fabric construction could be selected from either fabric weight classification in a 3 x 2 twill weave, using a plied warp with 4.0 twist multiplier in the singles, a warp cover factor of 19 and a filling cover factor of 12.0 achieved by using high pickage with fine filling yarns. A low warp twist multiplier would be desirable to achieve dimensional stability and to some extent attain acceptable abrasion resistance. However, as far as spinning and weaving are concerned (especially with the absence of warp sizing), the 3.5 twist multiplier used is inadequate. At a constant cover factor, it is desirable from both a dimensional stability and an abrasion resistance point of view, to have a great number of lightweight yarns in the filling. This, of course, results in increased cost for both commercial spinning and weaving operations. Of the three weave constructions studied, the 3 x 2 twill possessed the best overall abrasion resistance and was intermediate in dimensional stability performance.

From a dimensional stability point of view, singles filling yarns are better than equivalent count ply yarns and the higher cover factor fabrics evidence greater dimensional stability than those with reduced cover factors. These findings are in contradiction to those observed and known for cuff abrasion resistance.

DURABLE PRESS DENIMS WOVEN FROM POLYMER SIZED YARNS [SUMMARY]

by

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(Presented by C. O. Graham)

The Southern Utilization Research and Development Division is actively engaged in research to improve durable press and abrasion resistance properties of all-cotton durable-press fabrics. One approach has been concerned with the treatment of yarns with polymers selected to improve resistance to abrasion and possibly add to the smooth drying and crease retention characteristics of the finished fabric. This research involved treating both warp and filling yarns with the durable polymers before weaving.

This paper presents the results of recent research to improve the performance of all-cotton durable-press denim fabrics by polymer sizing the yarns. Most of the work centered around fabrics woven with untreated filling yarns. The investigations included variations in warp size formulations and durable-press finishes on the woven fabric.

Warp size applications were with durable polymers alone, such as polyurethanes and polyacrylates, combinations of durable and temporary polymers, and with the inclusion of crosslinking resins and catalysts in the warp size formulas. Durable polymers were used in amounts ranging from 3 to 16 percent solids. Temporary polymers, such as carboxymethylcellulose and polyvinyl alcohol, were used in amounts ranging from 2 to 4 percent solids. For the most part, size baths containing crosslinking resins had 3 percent solids of the crosslinking agent.

Fabrics woven from warp yarns sized with 8-percent polyurethane had 82-percent strength retention in the warp and 71-percent retention in the filling after a conventional pad-dry-cure treatment with a 14-percent solution of Permafresh 183.

A similar fabric woven from untreated yarns and given the same durable-press treatment (as the treated yarn fabric) had 60-percent strength retention in the warp and 57-percent retention in the filling. Stoll flex abrasion values for both warp and filling were three times greater for the fabric woven from the polymer treated warp yarns than for the fabric woven from the untreated yarn.

The inclusion of crosslinking resins and catalyst in the polymer size bath produced warp yarns with distinct characteristics; by this method temporary polymers such as PVA and CMC were converted to durable polymers.

Fabrics woven from yarns treated with this type formulation had good durable-press properties after crosslinking with only 2 percent solids resin add-on.

Durable-press finishes for the woven fabrics had various concentrations of the crosslinking resins and catalysts in the pad baths. The crosslinking resin varied from 1 to 5 percent solids add-on in the finished fabric. The effect of adding 1 percent CMC and 1 percent PVA to the crosslinking pad bath was also studied.

Warp yarns were sized with 8 percent solids polyurethane and 4 percent CMC. A denim fabric was woven from this warp yarn and an untreated filling yarn. The fabric was desized, scoured, and bleached. Portions of the bleached fabric were given three different crosslinking treatments: (1) a conventional pad-dry-cure using a 14-percent solution of Permafresh 183, a softener, and Catalyst X4; (2) pad-dry-cure using 14-percent solution Permafresh 183, a softener, Catalyst X4, and 1 percent CMC; and (3) pad-dry-cure using 14 percent Permafresh 183, a softener, Catalyst X4, and 1 percent polyvinyl alcohol. The fabrics treated with these formulations were tested for physical properties and laundry performance.

The addition of 1 percent CMC to the crosslinking pad bath greatly improved the physical properties of the crosslinked fabric. Strength retention for the fabric was 95 percent in the warp and 82 percent in the filling. Flex abrasion values were from 2 to 4.5 times greater than the untreated desized, scoured, and bleached fabric. The presence of CMC in the pad bath lowers crease recovery angles, wash-wear, and crease ratings. The addition of PVA to the crosslinking pad bath did not produce any improvement in the physical properties of the crosslinked fabric. The PVA did, however, improve crease recovery angles, wash-wear, and crease ratings substantially.

Cuffs were fabricated from the finished fabrics, pressed and cured for 8 minutes at 325° F. The cuffs were subjected to repeated laundering and tumble-dry cycles to test their resistance to edge abrasion and to evaluate wash-wear and crease ratings after laundering. Cuffs from the crosslinked fabrics woven from treated yarn had two to four times the number of cycles to failure than cuffs from the crosslinked fabrics woven from untreated yarn. Wash-wear and crease ratings were four or better in most all cases.

LIGHT SCATTERING STUDIES ON COTTON TO AID INSTRUMENT DESIGN

by

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Stanford Research Institute is currently completing work on *first generation prototypes* of two automated instruments supported by USDA's Southern Utilization Research and Development Division (SURDD) for determining data on fiber length and diameter and for counting neps and trash particles in cotton. Optical methods of detection were chosen for these objects because optical signals are easily converted to electrical signals for processing by logic circuitry. In addition, no intrinsic limitations on speed are imposed by this method of detection. Any speed limitations are imposed by the sample-handling system. One design objective for these instruments is relative simplicity to avoid high cost; this applies to both the optical system and the electronic circuitry.

The light scattering properties of some objects likely to be encountered in an opened cotton sample were studied to obtain information useful in the instruments' design. The objects studied were individual fibers, neps, and flocks and mats of fibers. Fibers and neps naturally received the more detailed study. Some polarization effects also were studied. The work was not exhaustive, in the sense of making measurements on many objects of the same class to attain high statistical significance.

Rationale. — The optical instruments' design does not involve high resolution scanning; only the simplest form of scanning is used. Consequently, interest was focused on intensity — and the effects of simple states of polarization on the intensity of all light that might enter the optical system — and on the angular distribution of the light about the scattering object. For this purpose, the Stokes vector representation is ideal for concisely expressing the desired information about the collected light. This vector is an ordered set of four real numbers expressing the intensity and state of polarization according to a preset convention. Since the field quantities characterizing the electromagnetic field of a flux of light can, and usually do, vary randomly in time and across the aperture of the viewing optical system, these quantities are usefully defined in the form of averages based on perpendicular components of the electric field vector.¹ The reference

plane chosen for this work is the scattering plane, the X component lying in the plane and the Y component perpendicular to the plane; the Z direction is the mean direction of propagation of the light in question.

The first component of the Stokes vector is proportional to the sum of the mean squares of the X and Y components for the convention used here and represents the average intensity of the flux. The second component is proportional to the difference between the mean squares of the X and Y components and represents the tendency toward linear polarization along one of the two axes. The second and third components are correlative in nature and are proportional to twice the average product of the magnitude of the two field vectors and the cosine and sine of their relative phase angle, respectively. The cosine (third) component measures the tendency toward linear polarization along axes at 45° or $90^\circ + 45^\circ$ to the X axis. The sine (fourth) component measures the tendency toward right or left circularly polarized light. The units of all these quantities can be any unit appropriate to intensity.

The effect of many optical devices^{2, 3} or of a scattering object⁴ on a light beam characterized by one set of values of the Stokes parameters produces an output beam whose Stokes parameters each are a linear combination of the original set of four. This may be formally expressed by matrix algebra, where the device or scatterer is represented by a 16-element matrix operating on the original Stokes vector to produce the vector characterizing the output beam, or the light scattered into a particular scattering angle. Therefore, a complete study of scattering from an arbitrary object can be regarded as an experimental determination of values of the components of a matrix as a function of object attitude and scattering angle.⁴

In principle, there are not 16 independent quantities to be determined. Because the elements are interrelated, there are only seven degrees of freedom, that is, seven independent constants characterizing the optical device or scattering object at a particular attitude (and scattering

¹M. Born and E. Wolf. Principles of Optics, Macmillan, New York, pp. 554-555, 1964.

²E. L. O'Neill. Introduction to Statistical Optics, Addison Wesley, Reading, Mass., pp. 133-156, 1963.

³W. A. Shurcliff. Polarized Light, Harvard University Press, Cambridge, Mass., pp. 109-123, 1962.

⁴H. C. Van de Hulst. Light Scattering by Small Particles, Wiley, New York, pp. 40-59, 1957.

angle). Elements of symmetry of a scattering object can reduce further the number of constants; for example, spherical symmetry of the scatterer implies four degrees of freedom. None of the objects studied here can be assumed to have elements of symmetry, because of the anisotropic nature of the cotton fiber, the nonsymmetric gross geometrical form; and the occurrence of some order in the fiber arrangement in such composite objects as neps.

Experimental apparatus. — The goniophotometer used in these studies is shown schematically in figure 1. The optical system is somewhat overcomplicated because components are confined to stock lenses. Measurement is by sensing and recording the position of the neutral wedge filter (supplemented by fixed, neutral filters to shift the accessible range) in the incident beam required to strike a balance between currents from the monitoring 929 phototube and the measuring 1P21 photomultiplier. The position of the filter is automatically adjusted for null by an electromechanical servoloop. The incident beam consists of a bundle of parallel beams formed by focusing an image of the source at infinity. These beams are made to pass through a common cross-sectional area at the scattering center where they form an image of a stop at that point. The angular divergence of the incident beam, nominally 3° , is governed by the opening of a stop at a point conjugate to the source. The incident beam's state of polarization is adjusted by a rotatable polarizer and quarter-wave plate. The scattered beam is analyzed by a polarizer and a quarter-wave plate, both of which are rotatable and interchangeable. Measurements consist of a series of angular scans at various settings of the polarizers and quarter-wave plates. These settings are calculated to cause various linear combinations of the unknown elements of the scattering matrix to determine the intensity viewed by the photomultiplier. The Stokes vector at the photomultiplier may be calculated by a matrix equation:

$$S_{pm} = M_a M_s M_p S_{inc}$$

where S_{pm} is the Stokes vector at the photomultiplier and S_{inc} is the Stokes vector of the light entering the polarizer, which is operated upon, in turn, by the known matrix representing the polarizer (M_p), the unknown matrix of the scattering object (M_s), and the known matrix of the analyzer (M_a). The photomultiplier responds to the first element of S_{pm} . Relative values of the scattering matrix can be calculated from the data as a function of scattering angle.

Scattering from neps. — Figures 2 through 5 show the scattering behavior of four neps in terms of relative values of M_{11} , the matrix element characterizing scattering from a completely unpolarized beam (550-nm wavelength). This resembles the scattering pattern of a large dielectric sphere. Only the four elements in the upper left corner of the scattering matrix were determined completely. These are concerned with scattering intensity and the interrelation of horizontally and vertically polarized light in the incident and scattered light. The scattering data for the four neps studies demonstrated a small but definite tendency to preserve these states of polarization. Values of these components given in table 1 demonstrate these findings.

Table 1. — Experimental results on scattering from neps

Nep No.	Angle (degrees)	M_{11} (arbitrary units)	$\frac{M_{12}}{M_{11}}$	$\frac{M_{21}}{M_{11}}$	$\frac{M_{22}}{M_{11}}$
1	18	540	-0.06	-0.02	+0.26
	36	220	-0.09	-0.02	0.25
	54	126	-0.08	-0.05	0.24
	72	89	-0.14	-0.08	0.24
	90	67	-0.14	-0.06	0.18
	108	58	-0.14	-0.08	0.20
	126	54	-0.08	-0.02	0.20
	144	52	-0.06	-0.01	0.21
2	162	52	-0.04	+0.02	0.22
	18	1,470	0.00	+0.04	+0.06
	36	670	+0.02	+0.01	+0.11
	54	310	-0.06	-0.08	+0.17
	72	230	-0.08	-0.06	+0.14
	90	169	-0.06	-0.06	+0.12
	108	140	-0.05	-0.04	+0.13
	126	120	-0.02	0.00	+0.14
3	144	110	0.00	0.00	+0.18
	162	110	+0.02	+0.02	+0.20
	18	1,870	-0.06	-0.04	+0.12
	36	820	-0.08	-0.02	+0.12
	54	470	-0.11	-0.05	+0.12
	72	320	-0.14	-0.06	+0.10
	90	260	-0.14	-0.06	+0.12
	108	220	-0.12	-0.05	+0.11
4	126	220	-0.09	-0.02	+0.14
	144	220	-0.08	0.00	+0.15
	162	240	-0.04	0.00	+0.15
	18	1,420	-0.35	-0.08	+0.25
	36	590	-0.37	-0.07	+0.24
	54	330	-0.42	-0.12	+0.25
	72	210	-0.42	-0.14	+0.24
	90	150	-0.44	-0.13	+0.21
	108	120	-0.44	-0.12	+0.20
	126	110	-0.41	-0.11	+0.24
	144	99	-0.39	-0.09	+0.24
	162	99	-0.39	-0.09	+0.24

Further investigation was directed toward discovering how close a nep's scattering matrix would approach the pattern imposed by spherical symmetry. Deviations were appreciable. However, these varied from nep to nep in a way suggesting fluctuations about spherical behavior as a mean, a reasonable behavior. There seemed to be nothing exploitable for nep discrimination.

The four elements of the lower right-hand corner of the matrix were not investigated. Since these elements deal with effects on 45° , linearly polarized and circularly polarized incident light, one may expect considerable activity. However, instrumental exploitation of such effects was regarded as too elaborate for a prototype instrument.

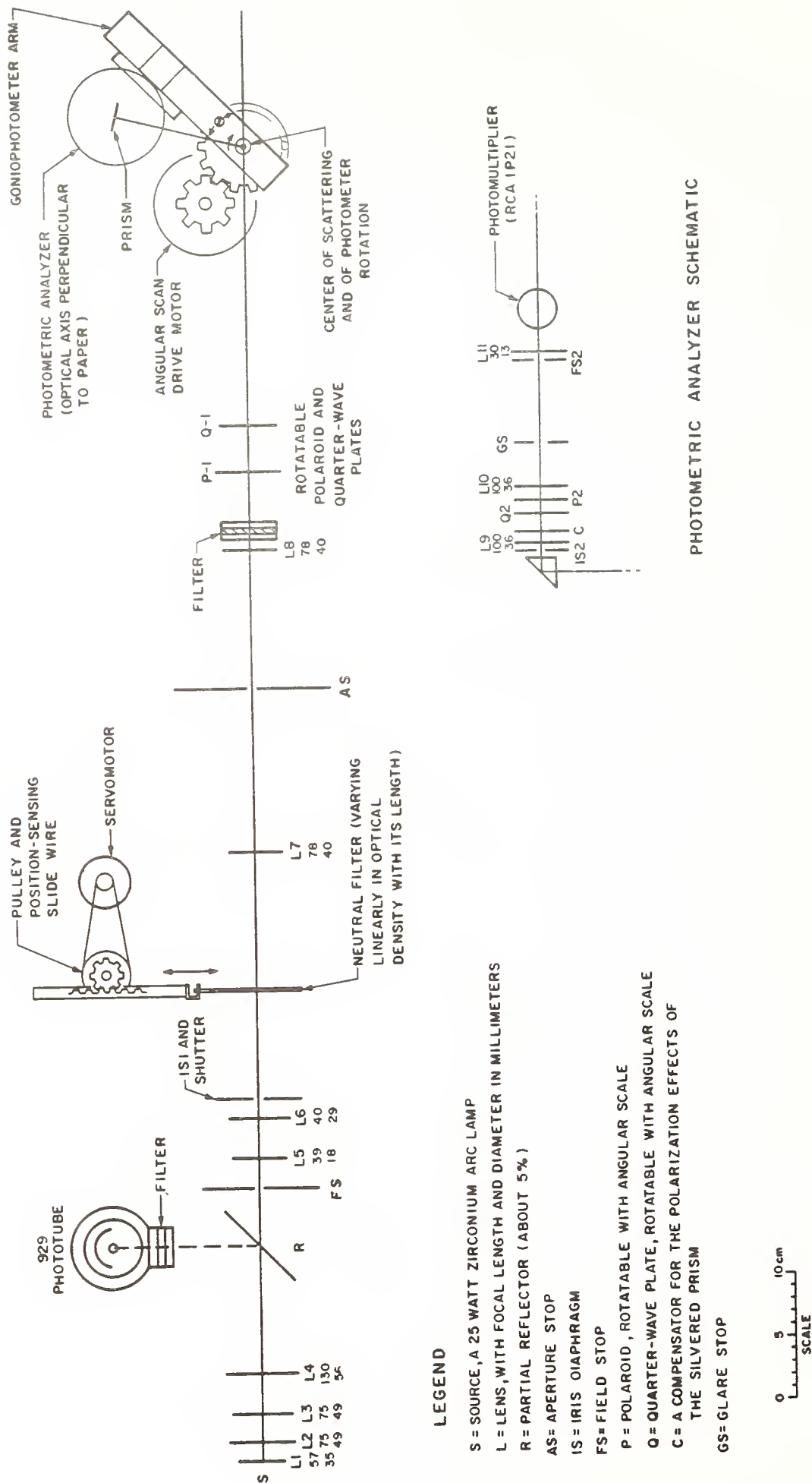


Figure 1. — Schematic Diagram of Optical System Used to Measure Light Scattering

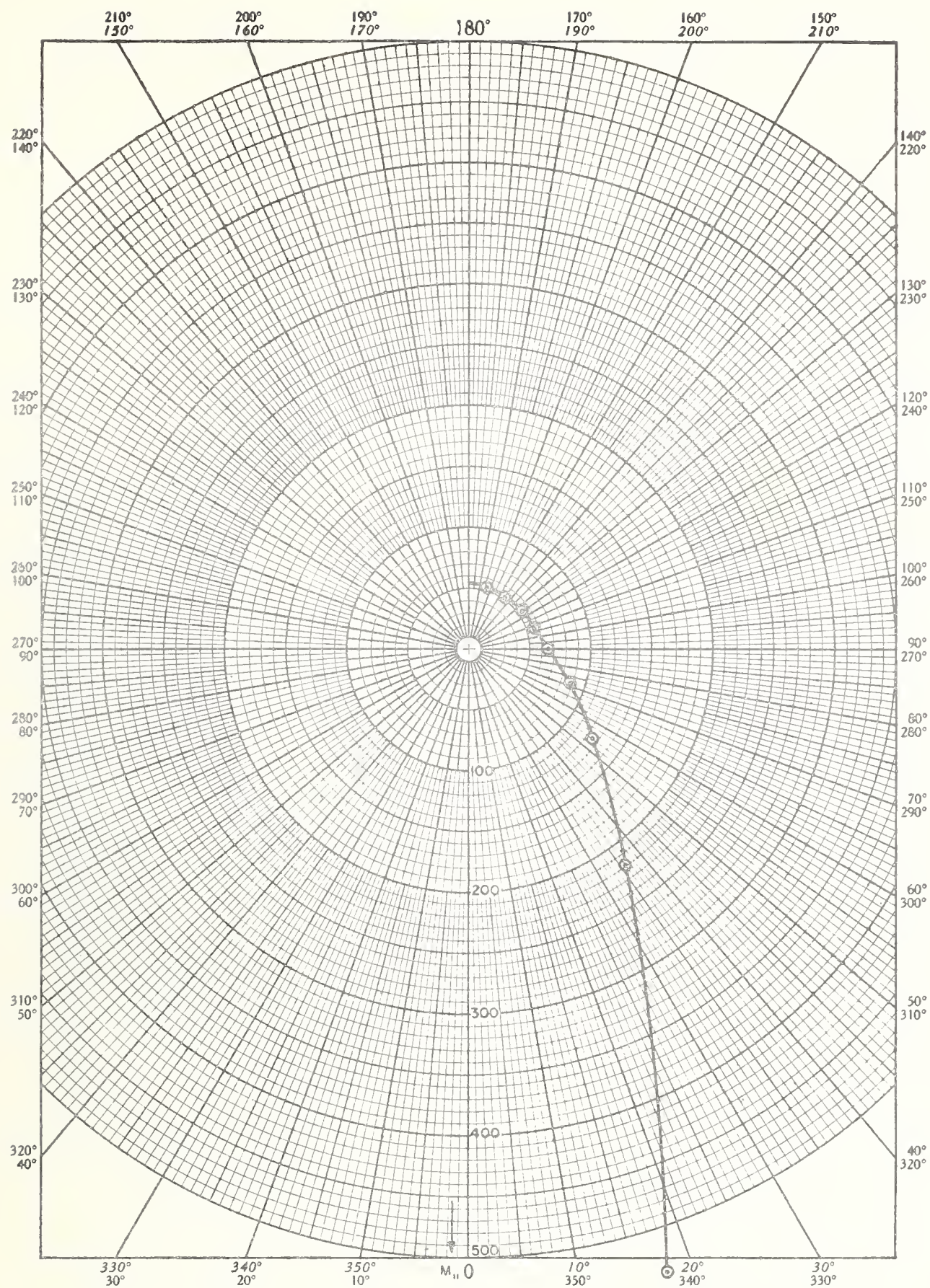


Figure 2. — Angular Dependence of Relative Values of Scattering of Natural Light (550 Millimicrons)
Nep No. 1

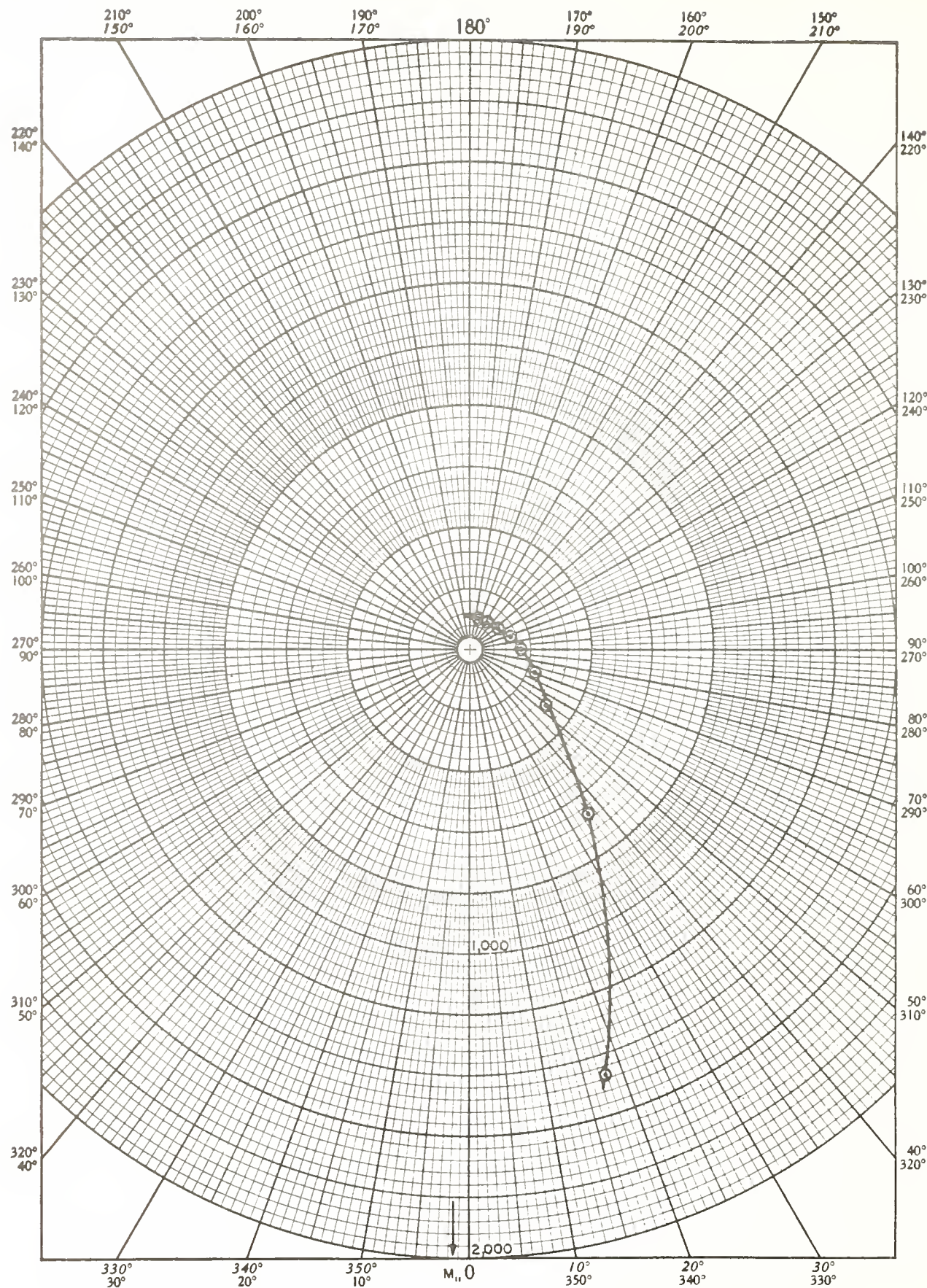


Figure 3. — Angular Dependence of Relative Values of Scattering of Natural Light (550 Millimicrons)
Nep No. 2

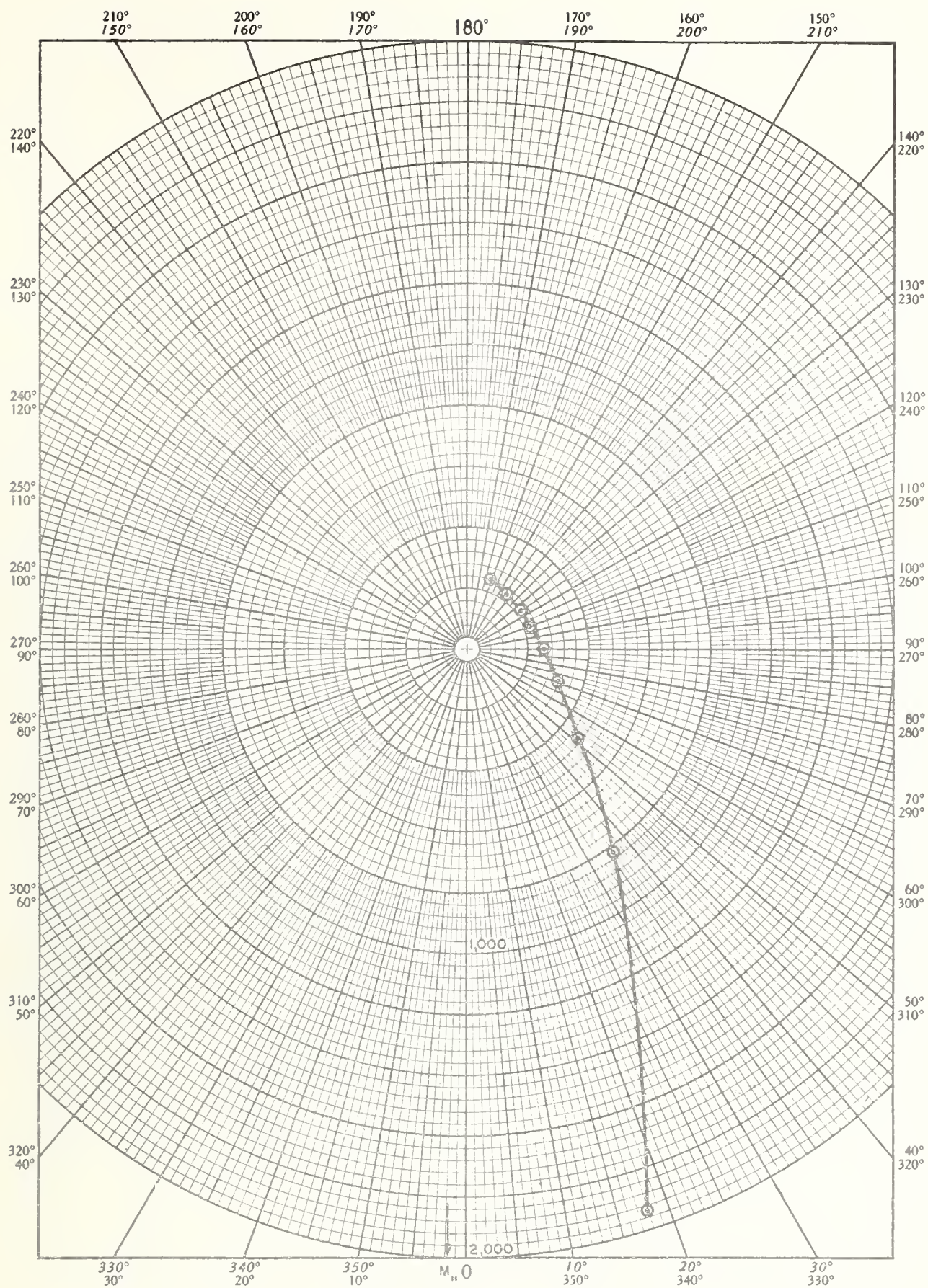


Figure 4. — Angular Dependence of Relative Values of Scattering of Natural Light (550 Millimicrons)
Nep No. 3

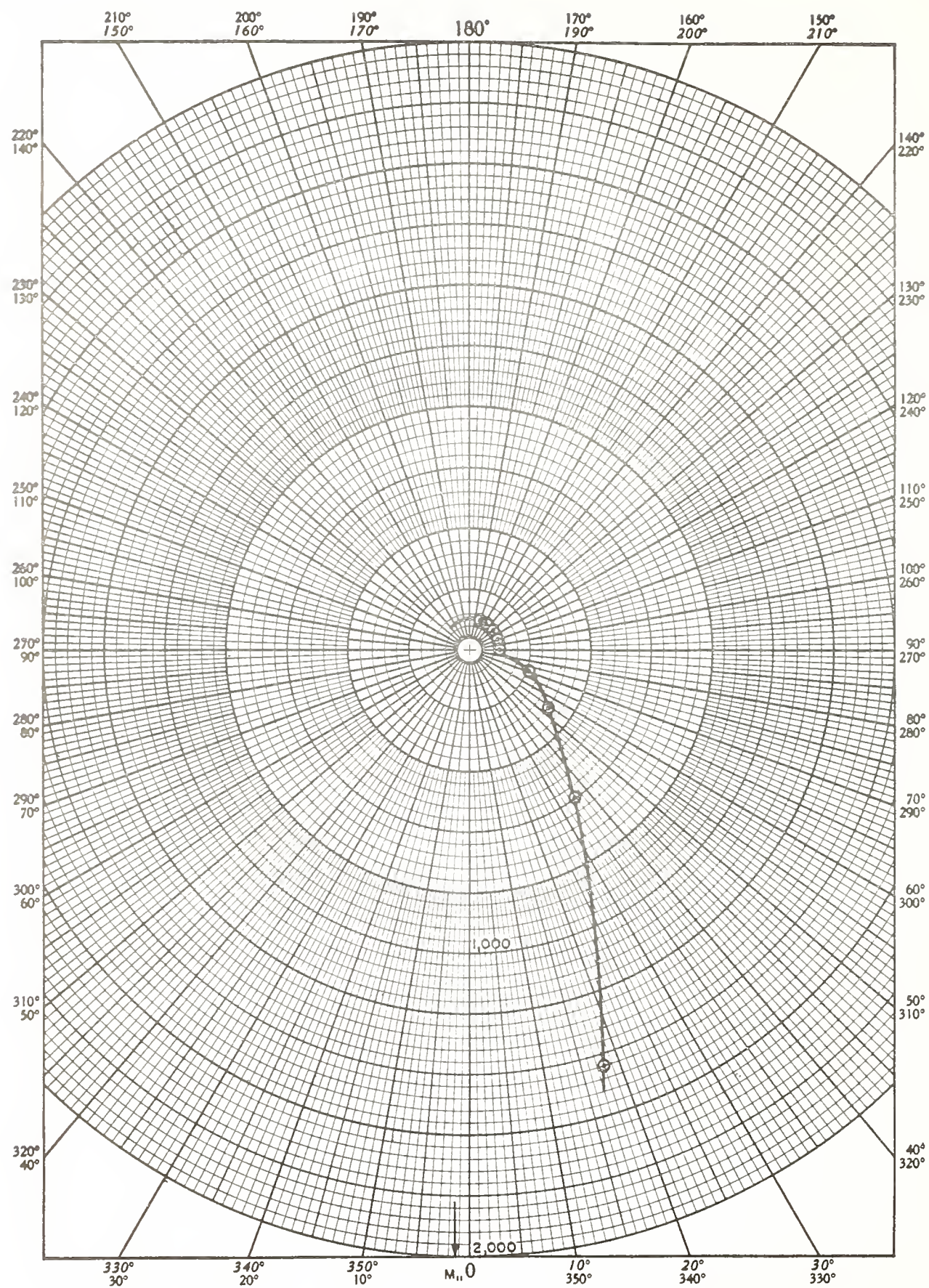


Figure 5. — Angular Dependence of Relative Values of Scattering of Natural Light (550 Millimicrons)
Nep. No. 4

The optice designed and built for the nep (and trash particle) counter reflect the above findings. Since no consistent effects were found for polarized light which might characterize neps, unpolarized incident light and no polarizing filters are utilized. The angular distribution of scattering from neps — as compared with the high forward scattering with fibers (as we shall see later) — showed that the contrast of neps against a background of fibers would be moderately improved by using back-scattered light to detect neps. The optical system, therefore, uses light scattered backward at a small angle with the incident beam. Incidentally, this is consistent with present practice in the visual counting of neps. As we shall see while discussing fibers, there is still some possibility of later incorporating polarizing filters for further improvement, to suppress back-scattering from fibers in the nep-counting background.

Scattering from flocks. — For the present purpose, flocks are defined as loosely packed, spheroidal agglomerates of cotton fibers such as might be encountered in an airborne, opened cotton sample. Two such agglomerates, measuring several millimeters across, were studied in the manner used for neps. The results for the matrix element M_{11} are shown in figures 6 and 7 and in table 2. In contrast with scattering from neps, scattering from flocks is more uniformly distributed in angle. Investigation of polarization effects showed that these flocks were good depolarizers. This contrasts with the behavior of the neps studied.

Table 2. — Experimental results on scattering from flocks

Flock No.	Angle (degrees)	M_{11} (arbitrary units)	$\frac{M_{12}}{M_{11}}$	$\frac{M_{21}}{M_{11}}$	$\frac{M_{22}}{M_{11}}$
1	18	1,930	-0.10	+0.06	+0.04
	36	1,520	-0.10	+0.02	+0.02
	54	1,400	-0.10	0.00	+0.02
	72	1,340	-0.10	0.00	+0.02
	90	1,290	-0.08	+0.02	+0.02
	108	1,210	-0.07	+0.02	+0.01
	126	1,120	-0.06	+0.01	+0.03
	144	1,130	-0.06	+0.02	+0.04
	162	1,200	-0.05	+0.02	+0.05
2	18	2,200	-0.05	0.00	+0.07
	36	1,210	-0.04	+0.02	+0.06
	54	840	-0.05	-0.01	+0.04
	72	580	-0.05	-0.01	+0.05
	90	530	-0.06	0.00	+0.04
	108	520	-0.06	0.00	+0.06
	126	570	-0.07	-0.01	+0.04
	144	610	-0.06	0.00	+0.06
	162	640	-0.04	+0.02	+0.06

Scattering from fibers. — Fibers were studied quite extensively, since one of the instruments measures fiber length and diameter using light scattering and the other detects neps in the presence of fibers. Several attitudes of one fiber were studied in great detail to find ways to

desensitize the length and diameter instrument to variations in fiber attitude about an ideal attitude on presentation of the fiber to the instrument.

The fiber study was terminated by a survey of selected scattering properties of single fibers of three quite different cottons. The selection of properties was on the basis of the results of the initial detailed study.

An Acala fiber was used as the specimen for the detailed study. The relative values of all 16 elements of the scattering matrix were determined as a function of scattering angle for various selected fiber attitudes relative to the scattering plane. The first cases studied were three rotational positions about the fiber axis, the positions being 45° apart with perpendicular incidence of the exciting light beam. A 1/16-inch long segment of the fiber was illuminated. The scattering of unpolarized light was mildly affected by these rotations (fig. 8). A maximum variation of approximately 25 percent, including experimental imprecision of the order of 10 percent, apparently was caused by the rotation. In contrast to the fiber composites previously discussed, this single fiber showed a pronounced tendency to operate on the states of polarization of the incident beam to produce polarized scattered light, an expected behavior. The only incident state of polarization producing enhanced scattered intensity was linear polarization with the electric vector in the scattering plane. The matrix elements that were definitely small at all experimentally studied scattering angles were M_{12} , M_{14} , M_{21} , M_{31} , M_{32} , and M_{41} . This implies the trivial conclusion that incident intensity does not affect the scattered state of polarization and the nontrivial conclusions that (1) the tendency toward perpendicular or parallel linear polarization in the scattered light depends on all polarization parameters of the incident light (2) the tendency toward 45° linear polarization of the scattered light depends on this same component, and the circularly polarized component of the scattered light is built up from all states of polarization of the incident light. Only M_{13} , M_{33} , M_{34} , and M_{43} showed apparent variation with rotation of the fiber about its own axis with perpendicular incidence of the exciting beam. M_{13} showed the least sensitivity of these three elements. This implies that any 45° linearly polarized component of the scattered light varies with rotation, and that if the incident light possesses an appreciable 45° linearly polarized component, then the circularly polarized component of the scattered light will vary with fiber rotation. These conclusions are merely indicative because they are derived from the study of one fiber of a single variety of cotton and because each matrix element depends on many experimental measurements of approximately 5 percent prevision; for example, M_{13} has nine, M_{33} twelve, and M_{34} eleven contributions from separate angular scans. However, one may safely say that polarization effects in fiber rotation are appreciable and that the optical design will have to allow for such effects. Another safe conclusion is that forward scattering geometry will yield the greater signal from fibers.

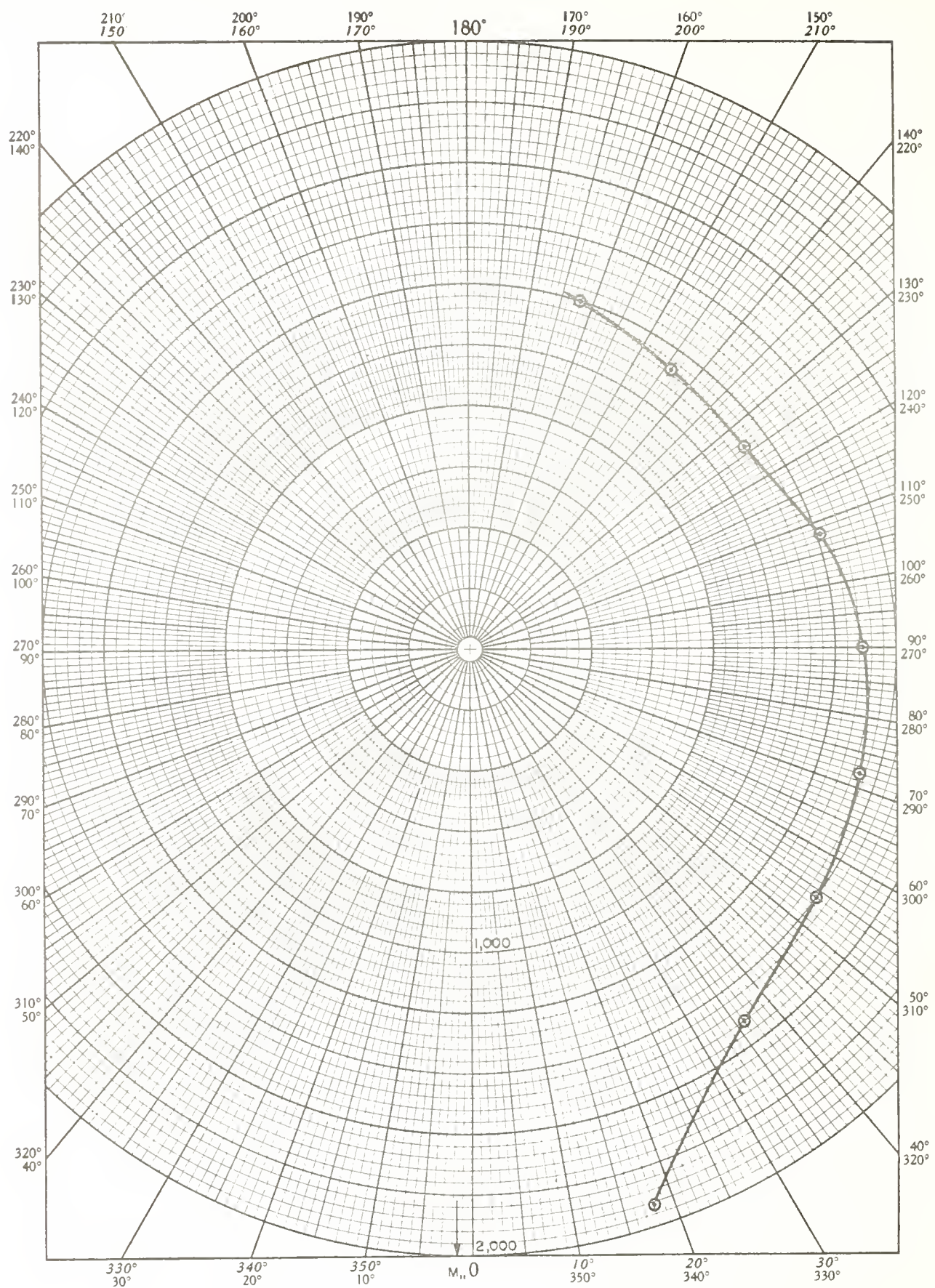


Figure 6. — Angular Dependence of Relative Values of Scattering of Natural Light (550 Millimicrons)
Flock No. 1

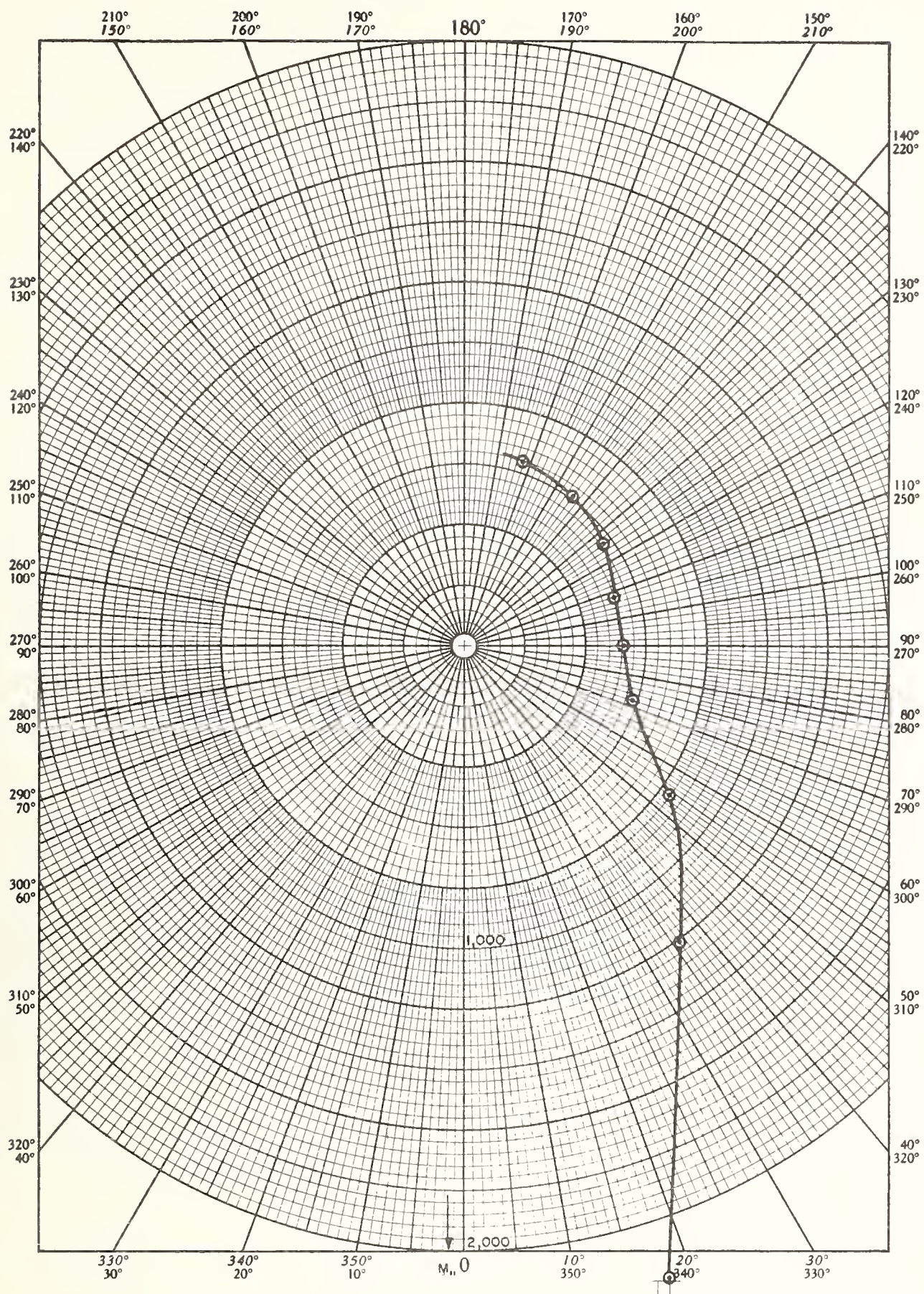


Figure 7. — Angular Dependence of Relative Values of Scattering of Natural Light (550 Millimicrons)
Flock No. 2

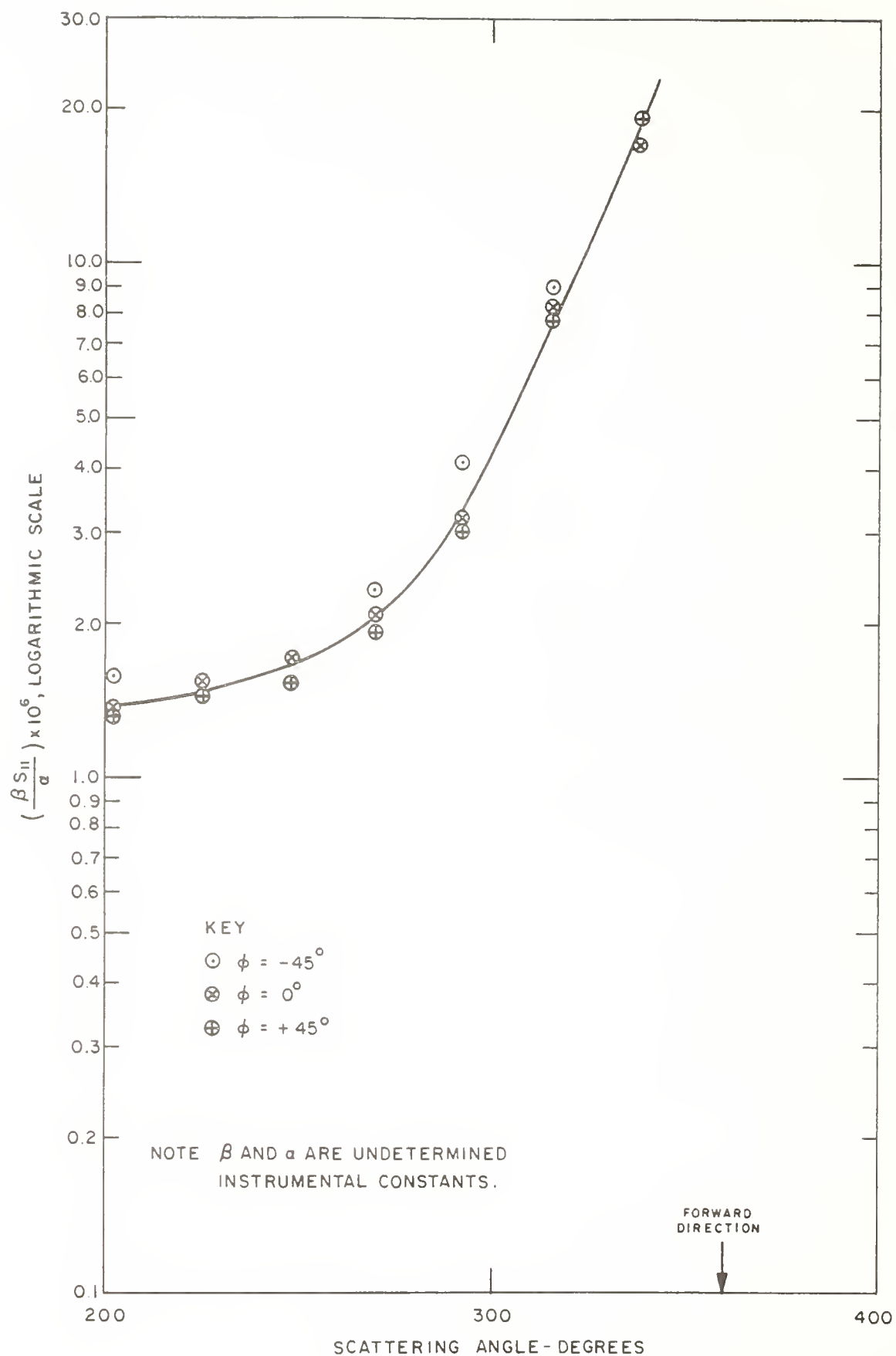


Figure 8. — Variation of Scattering Intensity with Scattering Angle for Three Angular Positions of the 1/16-Inch Scattering Fiber Segment

In any practical instrument, fibers will vary in their angular attitude relative to any scattering plane. This fact led to two studies of the scattering behavior of the same Acala fiber inclined at 30° from perpendicularity to the scattering plane. One study was with the fiber lying in a plane normal to the incident light. The other was for the mirror image of the first fiber's attitude, a plane perpendicular to the scattering plane and containing the incident beam serving as the imaginary mirror. The effect of the 30° inclination on scattered intensity from unpolarized incident light was pronounced, decreasing it as much as fourfold. The difference between the two attitudes was appreciable, up to 60 percent at a 90° scattering angle. These effects are shown in figure 9. The polarization parameters most affected by inclination were M_{12} and M_{32} , which assumed values other than zero on inclination of the fiber, and M_{34} , which was reduced to near zero by inclination of the fiber. M_{13} , M_{32} , M_{42} , and M_{43} changed their values appreciably between the two, mirror image, fiber attitudes. All these phenomena are consistent with the known optical properties of cotton fibers and with the theoretical behavior of cylinderlike, scattering objects.

The effect of the 30° inclination suggests concentration of scattered light about a plane perpendicular to the fiber's axis. Again this is consistent with theoretical results for cylindrical scatterers. However, since a cotton fiber is far from being a cylinder, it is better to have experimental results supporting a cylindrical model than to presuppose this sort of behavior. An auxiliary photographic study was made to confirm the hypothesized concentration of forward scattered light in an equatorial plane through the illuminated fiber segment. The pattern's existence was confirmed on the exposed film.

The design and construction of the optics of the fiber length and diameter instrument were based on the findings of the above study. It employs a large aperture, forward scattering system. A patch stop on the light collecting system blocks the incident light beam of small angular divergence. This forward scattering geometry takes advantage of the extensive forward scattering of the fibers. The large aperture is intended to capture the equatorial lobe of scattered light from segments of fibers passing through the incident light throughout a restricted but appreciable range of possible attitudes. This does reduce problems for the fiber feed system by loosening requirements on fiber attitudes.

Dependence of forward scattering on fiber diameter.
— Since one of the purposes of the prototype instrument is to obtain statistics on fiber diameter, a brief

investigation was carried out to determine a method for sensitizing the optical system to fiber diameter, a brief investigation was carried out to determine a method for sensitizing the optical system to fiber diameter. This brief study was intended to indicate the initial direction of development once the prototype instrument was built. Collecting the large amount of data necessary for statistically establishing the proper response to fiber diameter is obviously unprofitable using the goniophotometric method employed in these studies. An automated instrument facilitates the necessary collection and correlation of data needed to investigate various methods of sensitization.

Three single fibers were used, a mature Acala, a mature Deltapine, and an immature fiber of unknown variety that had a high nep potential. The mean diameters were in the ratio 1.0:0.70:0.55, respectively. The response to unpolarized incident light is shown in figure 10. Scattering is in order of diameters but definitely not directly proportional, an undesirable characteristic for the immediate object. The remainder of the measurements implicitly measures M_{12} , M_{21} , and M_{22} , but these elements were not calculated. Instead, four operationally defined measurements, directly related to simple polarizing arrangements that could be easily incorporated into a prototype instrument, were made as a function of forward scattering angle. These are shown in figures 11, 12, 13, and 14. In all figures except the first, Acala fiber was much the better scatterer. Figure 11 represents the horizontally polarized component of the scattered light from fibers illuminated with horizontally polarized light. In this case, the scattering is roughly proportional to the microscopically measured diameters. Consequently, this represents the first polarizing arrangement being tested in the instrument.

Conclusion. — These results have determined to a considerable degree the optics of the prototype instruments. The nep and trash instrument does reliably count neps. The response to trash particles has not been experimentally studied pending some further modifications. The fiber length and diameter instrument responds to fiber length and diameter. Sufficient data have not been accumulated to demonstrate whether it responds in the desired manner. It is fairly certain that fiber length can be determined; the most uncertain element is its quantitative response to diameter.

Most of our present and persistent difficulties are with the sample feed system.

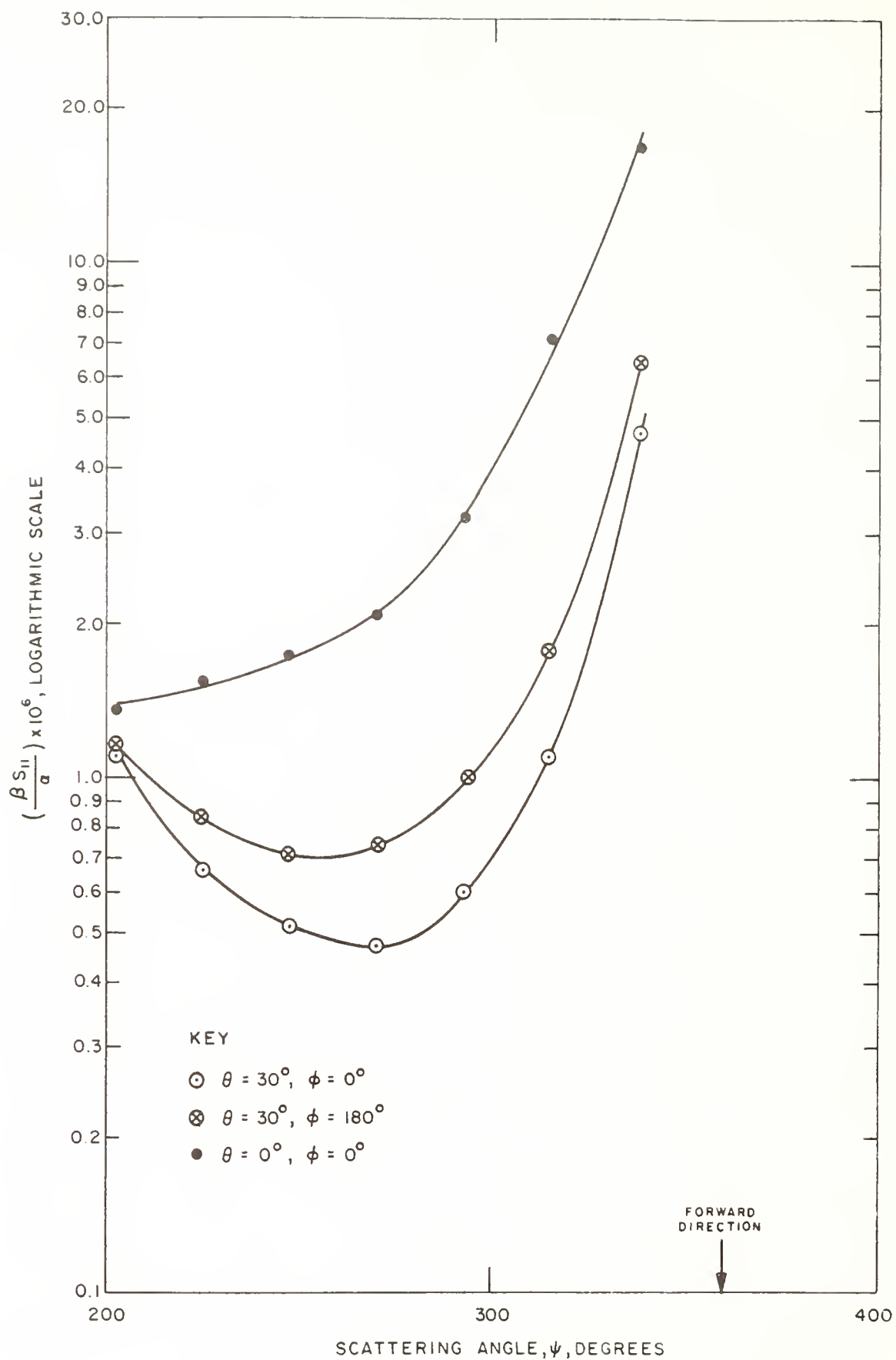


Figure 9. — Variation of Scattering Intensity with Scattering Angle for Inclined 1/16-Inch Fiber Segment

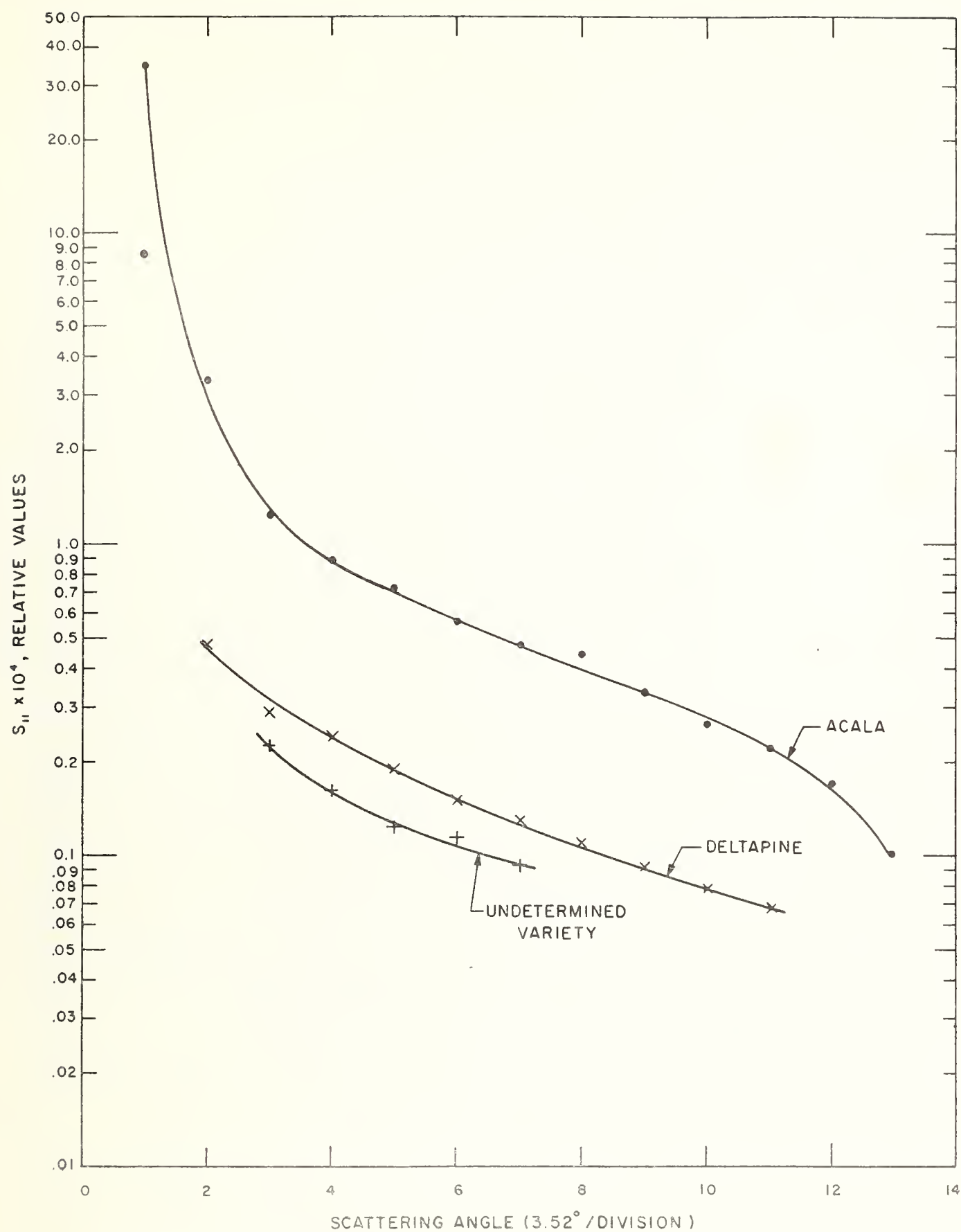


Figure 10. — Angular Dependence of Scattering for Three Cotton Fibers Using Unpolarized Incident Light and No Polarizing Filter in the Scattered Beam

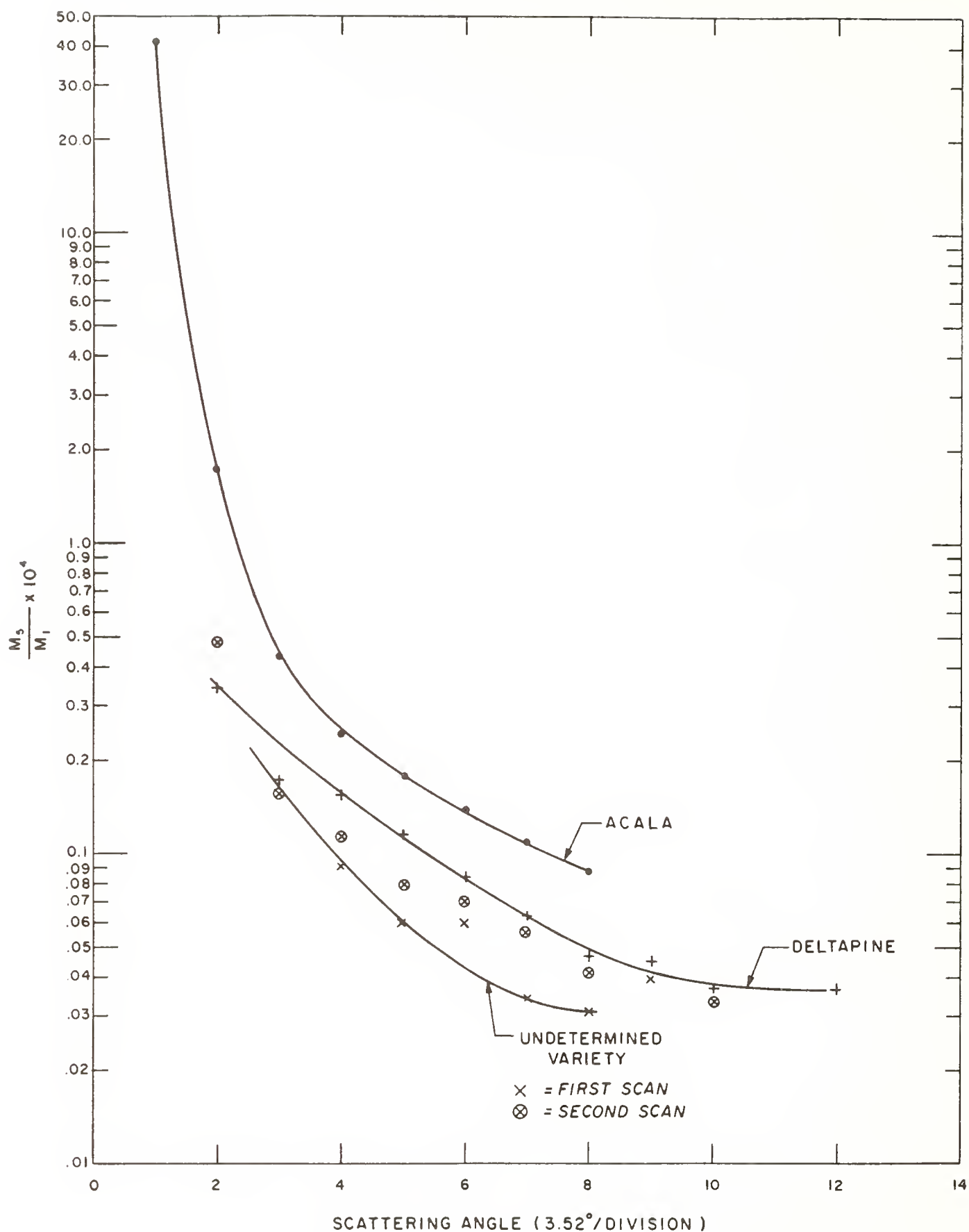


Figure 11. — Angular Dependence of Scattering for Three Cotton Fibers Using Horizontally Polarized Incident Light and Measuring the Horizontally Polarized Component of the Scattered Light

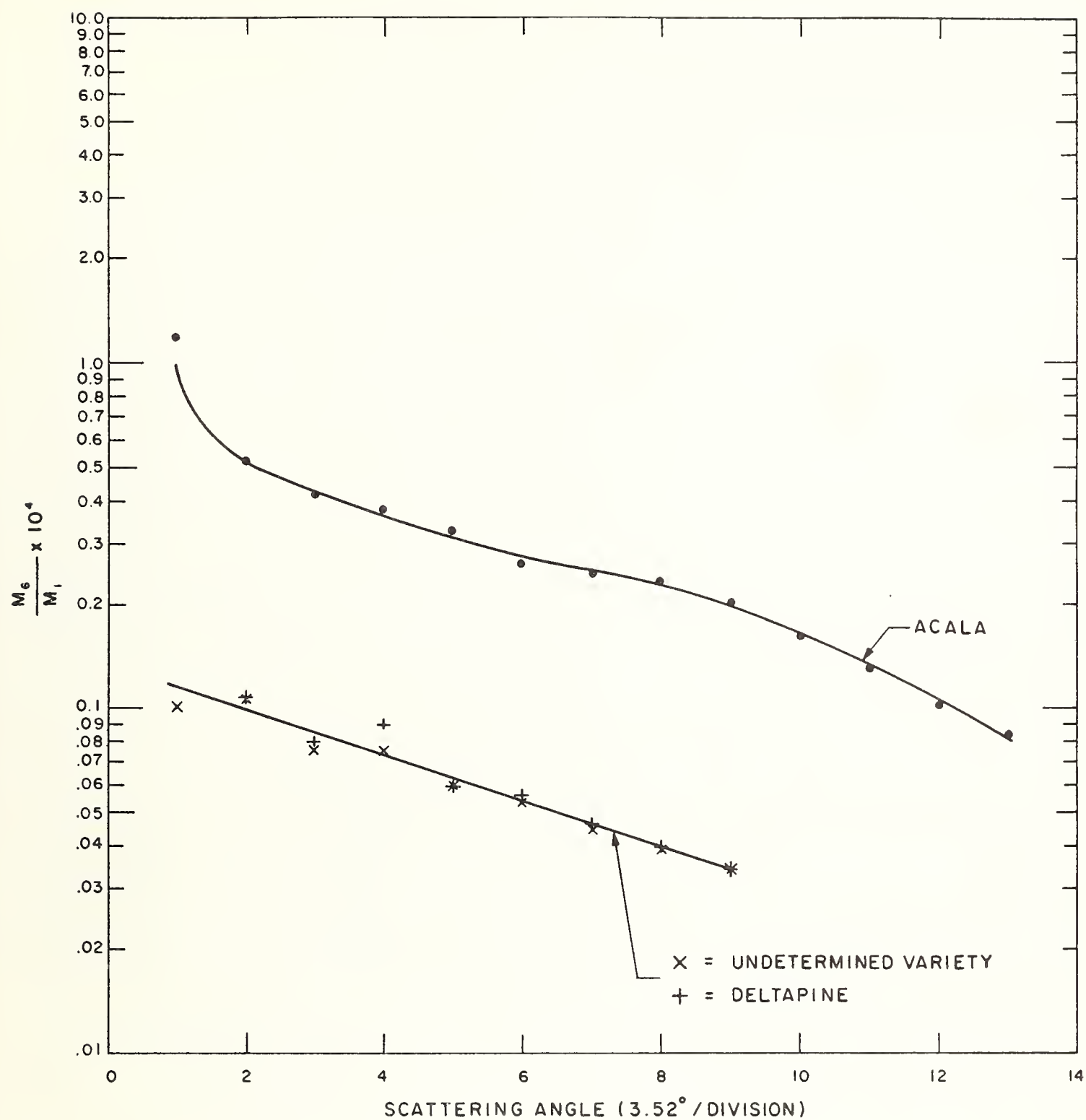


Figure 12. — Angular Dependence of Scattering for Three Cotton Fibers Using Horizontally Polarized Incident Light and Measuring the Vertically Polarized Component of the Scattered Light

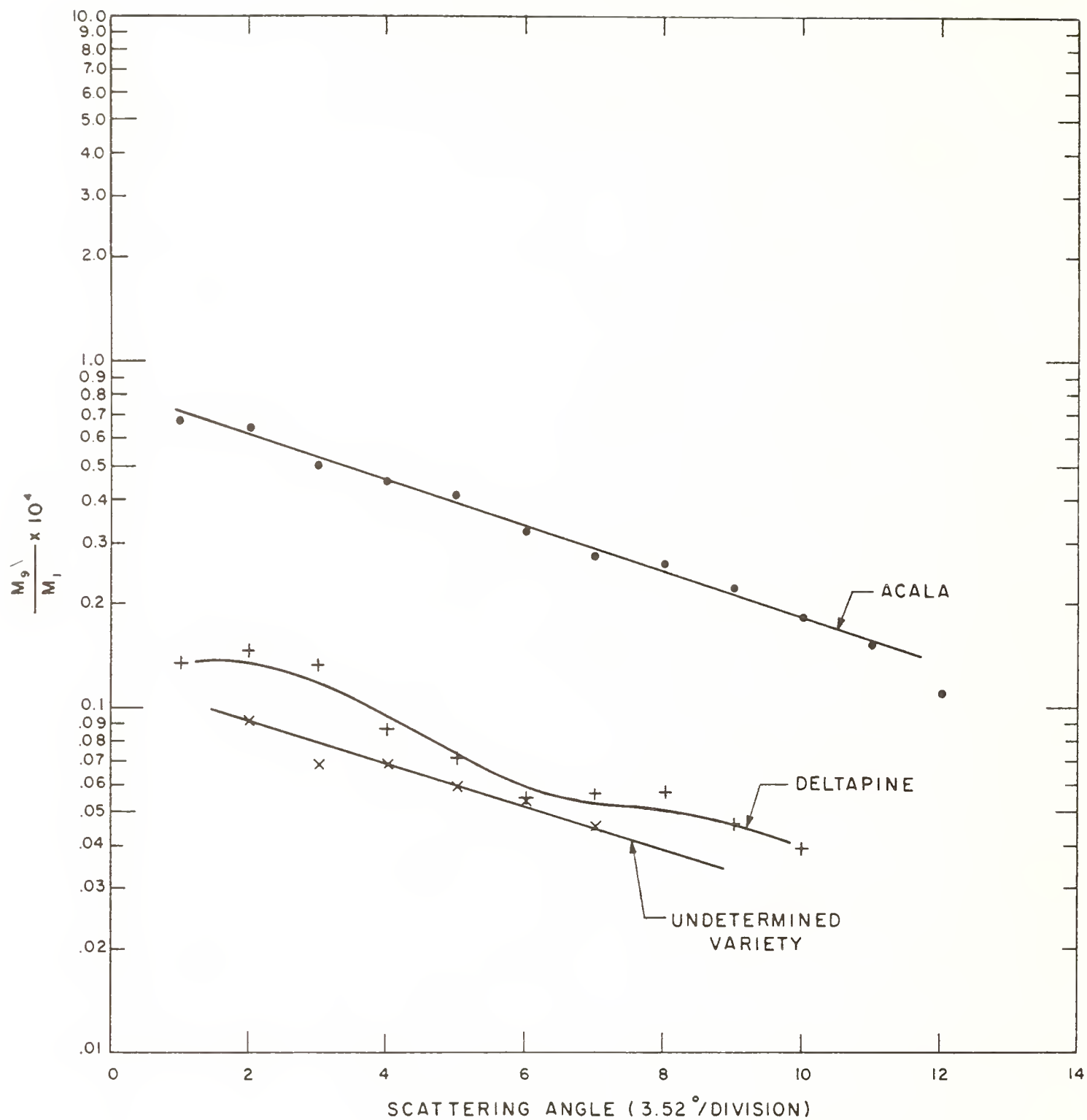


Figure 13. — Angular Dependence of Scattering for Three Cotton Fibers Using Vertically Polarized Incident Light and Measuring the Horizontally Polarized Component of the Scattered Light

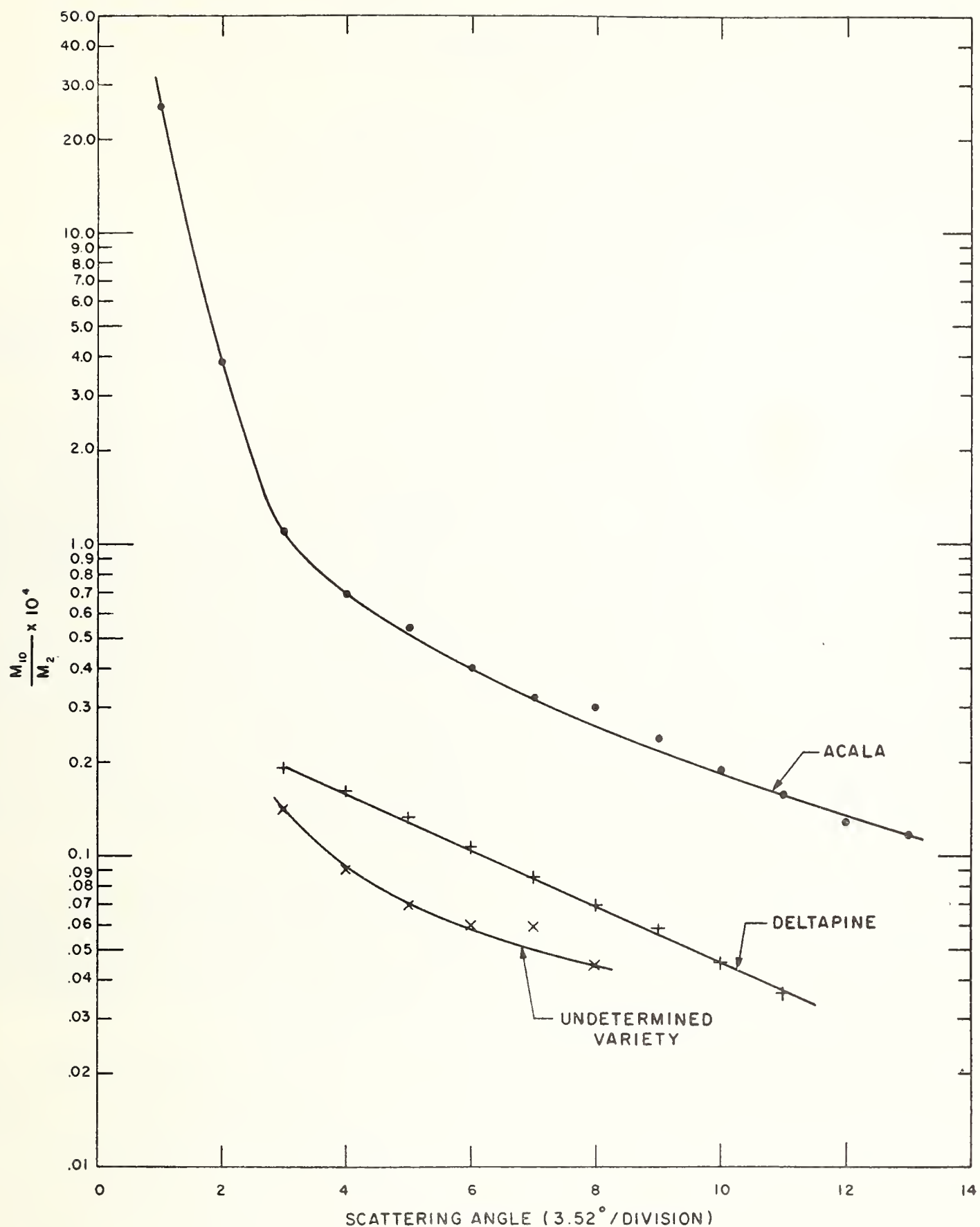


Figure 14. — Angular Dependence of Scattering for Three Cotton Fibers Using Vertically Polarized Incident Light and Measuring the Vertically Polarized Component of the Scattered Light

FIBERS, FIELDS AND FORCES [SUMMARY]

by

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(Presented by Albert Baril, Jr.)

A number of years ago in our textile machinery research, it was speculated that for the cotton textile market to be retained or increased, the textile processing system for cotton fibers would have to undergo radical change and a fundamentally new system be devised so that more products could be produced more rapidly at a lower cost. A modest start toward achieving this new system was initiated by selecting specific tasks that could be done in a new way. The first attempt was to fractionate fibers according to length by electrostatic field configurations. With ingenuity and some clever innovation, devices for accomplishing this separation were devised, built, and patented. At about this point in time, it was decided that a more comprehensive look at the basic concepts of the proposed new system should be undertaken. Little was known as to the action of fibers in force fields — either acoustic, aerodynamic, or electrostatic.

A comprehensive study was made of the effects of acoustic force fields on cotton fibers in both liquid and gaseous media on the physical and chemical properties of the fibers. No significant effects were found except for one narrow frequency band. After prolonged exposure at this frequency, compressive damage of the fiber occurred.

From the results of these preliminary experiments, it is questionable that the use of acoustic force fields for the performance of some of the textile processing steps, such as opening cotton tufts into individual fibers or to separate and destroy trash from the cotton, would be successful. These basic experiments did demonstrate that acoustic forces could be used on cotton since it did not damage the fibers and pointed to an area of research whereby the fibers could be manipulated directly into a nonwoven textile structure.

When evaluating the potential use of aerodynamic force fields for textile processing, one has to remember that the use of air for conveying tufts of cotton, separating trash from fibers, and doffing has been included in the overall process for a number of years. It was not until recently that the concept of using aerodynamic force fields to individualize, align, manipulate, and form fibers into a strand has been considered as the basis of a new textile processing system.

The main concern in the aerodynamic treatment of fibers is the response of the fibers to the flow field. In general, fibers are treated as cylinders in a laminar flow

field described by some form of Laplace's equation. The fiber reaction is in reality more complicated than the electrical analog due to aerodynamic drag and inertia, and hence does not follow the flow field lines, complicating the analysis of a fiber's behavior in a defined air flow.

Several defined air flow configurations were investigated and computer-analyzed. Those of interest include: flow in a straight duct with smaller ducts branching from it as a method of changing cotton concentration in a duct; the theoretical streamline about an ideal right angle corner that acts as a classifier, segregating particles by their sectional densities; vortex flows which impart to cotton tufts a strong outwardly directed radial force field potentially useful in opening and disentangling clumps; and dilation effects whereby cotton fibers are made to interact with the air inside of a given mass to produce outwardly directed forces on the fibers in the mass and impart an opening of the cotton tuft. Simple dilation chamber experiments were performed and a degree of opening was observed. From a theoretical dilation flow study performed, a set of governing equations was determined. Aerodynamic force fields show promise for some developments in cotton processing techniques, but restriction to nonturbulent laminar flow will be a limiting factor.

During our study of cotton fiber behavior in electrostatic fields, theoretical predictions of fiber behavior have conformed to a degree with experimental results, but numerous anomalous effects at critical stages warrant a more basic study of what is happening. One of the important questions that arise in such a study of the use of electrostatic fields is: with what forces do these fields act on the fibers?

Textile fibers may be considered dielectric bodies with bound and free charges. When such a dielectric is placed in an electric field, on each unit of its volume there is a force equivalent to the total force applied to the individual molecules constituting the volume. Due to the electric field a molecular deformation occurs, and, consequently, charges of opposite signs are formed and displaced relative to each other. As a result of the interaction of these coupled charges and the applied field, a force is applied to each element of volume of the dielectric. This force is known as ponderomotive as compared with the coulombic force (acting as a free charge) which may be imparted to a fiber by creation of a spare charge caused by corona discharge and by contact charging.

Movement of a fiber having a free charge (coulombic force) is obtained in homogeneous and nonhomogeneous fields. The force being exerted on a unit of charge or the fiber is proportional to the field intensity, and the direction of the fibers' movement depends on the direction of the field. Force is directly proportional to the charge on the fiber. Movement of fibers by ponderomotive force is possible in nonhomogeneous fields; only rotational motion is possible in a homogeneous field. This force, exerted on a unit volume of fiber, is proportional to the gradient of the square of the electric field intensity and depends on the fiber dielectric permeability. The direction of movement of fibers is toward the region of maximum field intensity.

The other force that must be considered is the mirror reflection force or that force acting on a fiber lying on or near to a conducting metallic surface. This force is calculated as that acting between charges distributed along the fiber and their mirror reflection, relative to the metallic surface.

A more precise concept of fiber action in particular field configurations under the influence of the described forces was obtained using the computer to map out the fields. Selected field parameters with given boundary conditions were given and by numerical integration the computer solved and plotted the equipotential lines for each configuration. By analysis of these plots the action of fibers in such defined fields is determined.

An example of this type of field mapping is that of a device designed to fractionate cotton fibers by length. This device consists essentially of a flat plate and a cylinder, with an electric field maintained between. Fibers are fed into the field and migrate according to the field intensity. By use of the computer-produced field map, the most advantageous location for fiber take-off could be determined and any necessary shaping of the field can be tried and verified without recourse to prototypes or laboratory models.

Another configuration of particular interest is that of a set of rings with angled discharge points placed around their inside circumference. When these rings are set up in line to form a duct and a successively higher potential is maintained on each of the rings, a method of conveying cotton fibers in an airless duct can be achieved. The computer field map of this configuration was necessary to determine how to distribute the discharge points and the potential gradient.

The judicious use of the interaction of force fields and fibers permits, in principle, the fractionation of fibers according to length, separation of impurities, orientation and straightening of fibers in the various stages of textile processing, bulking of yarns, conveying of fibers, orientation of fibers in the production of nonwoven materials, alinement of fibers in the flocking process, and even the cleaning of the air in the textile mill.

THE EFFECTS OF WEATHERING ON THE LAUNDERING
DURABILITY OF FIRE-RESISTANT COTTON FABRICS
[SUMMARY]

by

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(Presented by David A. Yeadon)

The fire resistance of household articles and of furnishings made from textiles is of serious concern for the consumer, the textile industry, and the government. The 1953 Federal Flammable Fabrics Act and its 1967 amendments are evidence of the government's interest to improve fire safety of flammable textile consumer goods. Industry, cautiously awaiting anticipated regulations from the government on flammability requirements for fire-resistant textile products, is eagerly seeking to improve fire-resistant treatments for textiles to overcome hazards of fire.

Many of the acceptable fire-resistant treatments consist of applying certain polymeric finishes to the cotton, of which a number were developed by the Southern Regional Research Laboratory. Most of these finishes are phosphorus and nitrogen-containing polymers based upon tris(l-aziridinyl)phosphine oxide (APO) and tetrakis(hydroxymethyl)phosphonium chloride (THPC). In general, these fire-resistant finishes on cotton fabrics are found to be durable to repeated machine washings and tumble dryings. Many polymeric materials are relatively stable to mild environmental conditions, but may be degraded or sensitized by energy exposures such as sunlight, ultraviolet, or heat. Fire-resistant fabrics are frequently used in drapes, curtains, furniture slipcovers, bedspreads, and so forth, which may encounter considerable sunlight during their normal useful life and are periodically laundered. However, contact with sunlight may activate the polymeric finish to reduce fire resistance or transform it to a state that is nondurable to subsequent washing and drying. This could be the case even though repeatedly washed and tumble-dried specimens had indicated no significant changes in their fire-resistant characteristics.

To investigate this point a series of tests were initiated to determine the effect sunlight, ultraviolet, and weather exposure followed by laundering would have on fire-retardant treated cottons. Flame-resistant fabrics were subjected to three types of exposures on a weather rack inclined at 45° from the horizontal and facing south beginning about the first of June. The three types of exposures were: (1) Under window glass to simulate sunshine falling on drapes, curtains, bedspreads, etc., through glass windows. To eliminate the leaching effect of

rain, the glass covered inserts were protected with a polyvinyl fluoride film. This arrangement allowed screening by the glass and film of more than 2/3 of the harmful ultraviolet rays below about 3,350 angstroms while letting some 70 percent of visible light through. (2) Under vinyl fluoride film only to determine the effect of sunlight without rain. This permitted more than 70 percent of the ultraviolet and 75 to 80 percent of the visible light to fall on the fabrics. (3) Under direct weathering conditions to compare with the above. Periodic evaluations for flame resistance were made by the vertical flame test on samples exposed up to 6 months, as removed from the weather rack and after five and 25 washing-tumble drying cycles. Phosphorus and nitrogen contents of the fabrics were evaluated.

THPC-type fire-retardant treated cotton fabrics were selected for these experiments, which included two commercially treated and four laboratory-treated fabrics. The laboratory-treated fabrics were finished with (1) THPC-methylolmelamine (MM)-urea; (2) APO-THPC; (3) tetrakis-(hydroxymethyl)phosphonium hydroxide (THPOH)-ammonia; and (4) THPC-MM-urea with 0.2 wt. percent of an ultraviolet screening agent deposited on the treated cotton. This screening agent absorbs the ultraviolet below 4,000 angstroms and was intended to reduce the effect of this radiation on the fire-retardant polymer.

Exposure of these treated cottons to sunlight and weathering indicated a marked change in the durability of their flame-resistant treatments. Because in initial tests the THPOH-ammonia sample did not seem representative for this type of treatment, results with this sample were eliminated from the weather rack exposure-laundering part of this study.

All other fabrics initially passed the vertical flame test with 25 washing-tumble drying cycles. Exposed under glass for 6 to 10 weeks all fabrics failed by 25 cycles, with one commercial fabric failing in only 1 week's exposure when washed 25 times. With 3 weeks' exposure this same commercial fabric failed by five launderings, while the other commercial and the APO-THPC fabrics were exposed 10 weeks and the THPC-MM-urea fabric was exposed 14 to 18 weeks before failing the vertical test by the 5-cycle laundering level. No advantage was observed

for the treated fabric with the UV screening agent. These results indicate that these flame-resistant treatments on fabrics when exposed to sunlight for about 3 months, even through glass, and laundered lose their durability by five laundering cycles. Moreover, one of the commercially treated fabrics did not pass flame resistance when laundered only one time after 18 weeks of exposure under glass. Consequently, under these conditions, articles made from such fabrics could become potential fire safety hazards in a few months.

The above results indicate the deleterious effect of exposure to sunlight on the durability of these flame-resistant treated cotton fabrics, particularly when laundered after exposure. In view of this, the durability of flame-resistant garments is questionable for those instances where flame-resistant articles are exposed to the sunshine in outdoor line drying after washing. Although many tumble dryers are in use today, it is believed that a significant number of households do not possess dryers and are compelled to use outdoor drying. Also, many housewives prefer to outdoor dry garments rather than machine dry, at least on periodic occasions to restore garment "freshness." In these cases more frequent washings may hasten the decrease of flame resistance caused by activity of the sun. Finally, many household articles and garments are pressed before use, and exposure to such thermal conditions may likewise affect the finish. Therefore, a test series was set up to determine the effect outdoor line drying and hot pressing would have on the durability of flame-resistant treatments on cotton fabrics.

For these experiments the treated fabrics selected included in addition to the two commercial and three laboratory THPC flame-resistant fabrics, a third commercial THPC flame-resistant fabric and a commercial non-THPC flame-resistant fabric (a phosphonate-type treatment). The THPC-MM-urea laboratory-treated cotton with the UV screening agent was not included in these line-drying tests, and another THPOH-ammonia laboratory-treated cotton fabric sample, which was indicated to be a satisfactory treatment, replaced the sample that had been used for the weather rack exposure-laundering study. Flame resistance was periodically determined on line-dried and line-dried and pressed samples. Control samples were tumble-dried and tumble-dried and pressed. Because these outdoor line-drying evaluations were unfortunately conducted during midwinter months, the effects from sunlight

exposures are minimal. Even so, the results show that the durability of the treatments on some of these fabrics was affected by outdoor line drying or thermal exposure.

All of the commercial THPC flame-resistant fabrics pass the vertical flame test through 50 washing-tumble drying cycles, but when washed and line-dried two failed by 12 to 16 cycles and the other by 25 cycles. In a like manner, the laboratory THPOH-ammonia-treated cotton although passing the flame test after 25 to 30 tumble dry and tumble dry-pressing cycles, failed to pass by only six wash-line dry cycles. It seems evident that the flame-resistant finishes on these fabric samples were particularly sensitive to degradation on outdoor line drying.

The durability of the laboratory APO-THPC and the commercial non-THPC flame-resistant fabrics in these tests are affected somewhat differently. The APO-THPC fabric samples showed flame-resistance that was borderline to failing by 25 to 35 tumble dry-pressing and tumble dry laundering cycles, and also by 45 to 50 outdoor line dry and line dry-pressing laundering cycles. Somewhat comparably, the phosphonate-type treated fabric fails in flame resistance by 13 washing-tumble dry-pressing cycles and 23 to 33 washing-line dry and pressing cycles, but apparently is still flame resistant after 50 tumble dry and line dry laundering cycles without pressing. Thus, these two treatments appear to be affected by thermal exposure during drying and pressing.

Of all the fabrics in these line dry tests, only the laboratory-treated THPC-MM-urea fabric passes the vertical flame-resistance test through 50 cycles of all types of drying and pressing.

In summary, limited evaluations with selected THPC-based flame-resistant cottons indicated most can pass customary washing-tumble dry flame-resistance durability tests, but show reduced durability to laundering after weathering, sunlight or thermal exposures. As a consequence, a flame-resistant article which may pass usual durability tests could harbor a potential fire safety hazard if subjected to sunlight or thermal exposure during use or laundering. More meaningful durability evaluations, incorporating protective UV absorbing agents, and more durable flame-retardant treatments for cotton are needed. Investigations of these areas are in progress.

PHOTOCHEMICAL AND THERMAL DEGRADATION OF SELECTED FLAME RETARDANTS [SUMMARY]

by

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(Presented by L. W. Mazzeno, Jr.)

With the passage of legislation that will eventually establish regulations and requirements that household and apparel fabrics be flame retardant, research in this field has been greatly intensified. Finishes durable to normal laundering and with retention of original physical properties will be quite in demand. Over the past three decades research has produced several finishes that show much promise for acceptance. In fact formulations based on tetrakis(hydroxymethyl)phosphonium chloride (THPC) are being applied for apparel and household textiles. Durability to 50 to 100 home-type launderings and tumble dryings can be achieved. Physical properties, while reduced, are acceptable in medium to heavy fabrics. More recently a new finish, the tetrakis(hydroxymethyl)-phosphonium hydroxide (THPOH) finish has been recommended for lightweight fabrics.

To date no low add-on (30 percent or less) finish has been developed that is durable to outdoor weather exposure. The current outdoor finish requires a minimum of 35 to 40 percent add-on and is not suitable for many uses, particularly household and apparel fabrics. Durability of flame resistance to outdoor weathering is becoming more important for such items as draperies, outdoor garments, and other apparel where line drying is to be practiced.

The most extensive report on outdoor exposure studies of flame-resistant fabrics is that of Bullock and others. Their results indicate that cleavage occurs in polymer-to-cellulose bonds and polymer-polymer bonds. With the THPC-type finish polymer-cellulose bonds rupture and intact polymer leaches out. In the APO-THPC they believe fragmentation of polymer is more likely.

Many reports appear in the literature on the thermal degradation of cellulose with and without flame retardants. This work was almost exclusively carried out at temperatures where decomposition of the cellulose substrate occurs. A primary conclusion in all cases is that the presence of the flame retardant lowers the decomposition temperature of the cellulose.

In the present study principal concern is with the changes occurring under conditions more closely related to the use of flame-retardant articles. Treated fabrics and

films formed from flame-retardant formulations have been exposed to U.V. light. Water extracts of these fabrics have been compared with the exposed films and with extracts from weather-exposed fabrics.

Fabrics used in this study were treated in the pilot plant with APO-THPC, THPOH-TMM-urea, and THPC-TMM-urea. Commercial fabrics were of the THPC- and phosphonate-type flame retardants. All were undyed. All films were cast on Irtran (ZnS) plates. Drying, curing, and exposure of films to U.V. were made with the film on the plate. Extractions were performed by boiling a swatch of fabric in distilled water for approximately 10 minutes and concentrating of the extract on a steam bath. The concentrates were transferred to Irtran plates and air-dried followed by drying over P_2O_5 .

The IR spectrum of a THPC-TMM-urea fabric after 18 weeks' outdoor exposure was remarkably similar to that of the unexposed fabric. Despite this similarity, the original sample had excellent flame resistance while the exposed sample burned entirely. Elemental analysis indicated that exposure caused loss in phosphorus content to a point well below the minimum for flame retardancy. Exposure of the same fabric for 18 weeks under glass did not destroy the flame resistance. The fact that the spectra of these fabrics before and after exposure were essentially identical would support Bullock's postulation that the intact polymer leaches out. However, these spectra are not identical to a dried and cured film of the THPC-TMM-urea formulation. Also, the spectrum of a water extract of the 18-week weather-exposed sample is comparable with that of an extract of a THPC-TMM-urea fabric exposed to U.V. light (thoroughly extracted with water before U.V. exposure). No appreciable extract comes off before the U.V. exposure. Another interesting observation made at this point is that a water extract of a U.V.-exposed THPOH-TMM-urea-treated fabric gives essentially the same spectrum.

To determine the agent in the formulation causing the change on exposure of the THPC-TMM-urea fabrics to U.V. or weather, several films of the formulation were analyzed. All films were dried, cured, and exposed to U.V. No changes were noted in a THPC-TMM-film. When urea was included, however, definite changes were noted

at each stage. Also, the changes in the spectra of THPC-TMM-urea and THPC-urea films were comparable. From this the authors concluded that the urea is in some manner responsible for the deterioration of the finish. Ultraviolet light appears to convert the flame-retardant polymer in the cotton to a water soluble form and this slowly leaches out on exposure to weather.

Similar studies are underway on APO-THPC, THPOH-NH₃, THPOH-TMM-urea, phosphonate-type finishes, and some commercial THPC-type fabrics, and will be the subject of a subsequent publication.

The THPOH-NH₃ finished fabric appears, from the work of Yeadon, to be most susceptible to deterioration on line drying. Suitable films of the polymer could not be prepared because a white polymer deposits on addition of gaseous ammonia or of NH₄OH to the THPOH. A sample of the THPOH-NH₄OH, washed free of salt was analyzed (IR) before and after U.V. exposure. The only notable

change was an intensification of the 1650 cm⁻¹ band. This is the region of the spectrum where NH, NH₂, or CNH groups are expected to be found. The same change is observed before and after exposure of a THPOH-NH₃ treated fabric.

In the course of heating films of THPC-TMM-urea, there was some indication that the changes brought about by U.V. exposure may be similar to those by prolonged heating. A preliminary heating trial, up to 8 hours at 160° C., failed to cause any significant change in phosphorus content or the flame resistance in any of the following treated fabrics: APO-THPC, THPOH-TMM-urea, THPC-TMM-urea, and three commercial THPC-type fabrics. The phosphonate-type while retaining its phosphorus content lost its flame resistance after 4 hours' heating followed by one laundering. Heating of these samples (except the phosphonate) in an autoclave at 100 p.s.i. steam for 1/2 hour destroyed the flame resistance in all but the APO-THPC fabric.

PROTECTION OF FLAME RETARDANTS FROM ACTINIC DEGRADATION [SUMMARY]

by

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(Presented by Ralph J. Brysson)

Recent studies at the USDA's Southern Regional Research Laboratory have indicated that several of the "durable" flame-retardant treatments for cotton fabrics are extremely sensitive to sunlight exposure and lose their flame retardancy after a relatively few home laundry-line dry cycles or after brief exposure to sunlight followed by laundering. This Laboratory has had extensive experience in pigments and their effect in reducing the deleterious effect of light on exposed cotton fabric. It was reasoned that possibly a similar reduction in the apparently light-induced degradation of some flame retardants could be achieved by the application of suitable light-screening pigments.

Four commercially finished, flame-retardant cotton fabrics were obtained from different finishing concerns. To maintain as complete objectivity as possible, no description of the fabric treatment other than that it was a standard treatment being sold as a durable flame retardant was required. The fabrics were all white cotton. They were a combed twill (A), a twist twill suiting (B), a flannel (C), and a jean cloth (D).

In addition, four laboratory pilot-plant produced samples were obtained. These were all applied to a scoured, desized, and bleached 7.6 oz. white cotton sateen. The treatments used were tetrakis(hydroxymethyl)phosphonium hydroxide-ammonia cure (THPOH-NH₃), tris(1-aziridinyl)phosphine oxide-tetrakis(hydroxymethyl)phosphonium chloride (APO-THPC), THPC-urea-trimethylolmelamine (THPC-U-M), and THPOH-urea-trimethylolmelamine (THPOH-U-M). For comparison, two olive drab dyed cotton sateens treated with THPOH-NH₃ and THPC-U-M were included in the study.

To test the hypothesis that sunlight screening pigments that had been shown to protect cotton fabric from light damage would also retard the light-induced degradation of flame retardants, parts of each of the eight white flame-retardant fabrics were aftertreated with pigmentbinder combinations. The pigments were a commonly used blue printing pigment, phthalocyanine blue and rutile titanium dioxide. The white TiO₂ effectively serves as a "colorless" finish for white goods. The pigments were applied at approximately 2 percent based on fabric weight. A vinyl-acrylic resin (3 percent by fabric weight) served as the binder.

The conditions of test were wash and gas dryer tumble dry (W-TD) with standard vertical flame tests made at 0, 25, and 50 cycles. Wash-line dry (W-LD) samples were line-dried outdoors after machine washing and were tested for flame retardancy at intervals of 5, 10, 15, 20, 25, 30, 40, and 50 cycles. In a related series the pigmented and unpigmented samples were exposed for 2, 4, and 6 weeks and flame tested after 5, 25, and 50 wash-tumble dry cycles. Because several of the flame retardants failed to pass the flame test after 2 weeks of exposure, an additional set of exposures for these samples was made. This consisted of exposure for 2, 4, and 7 days with flame testing after 1, 5, and 25 wash-tumble dry cycles.

RESULTS

Commercial Sample A (combed twill) unpigmented passed 25 W-TD cycles but failed at 50 cycles. On line drying it failed at 15 cycles. The white-treated sample unexpectedly failed at 10 W-LD cycles. The blue-treated sample showed evidence of protection and did not fail until after 25 W-LD cycles. In the continuous exposure followed by W-TD cycles the protection afforded by the pigments was more evident. Unpigmented samples failed after 5 and 1 washes after 2 and 4 days' exposure. The white samples withstood 25 washes after 2 days' exposure, 5 washes after 4 and 7 days' exposure. The blue sample passed 25 washes after 2 and 4 days and 5 washes after 7 days.

Commercial Sample B (twist twill) untreated failed after only 15 W-LD cycles; the blue and white pigmented samples did not fail until after 30 cycles. On continuous exposure for 2 weeks the untreated sample failed after five washes while the blue and white samples were flame retardant after 25 wash cycles.

Commercial sample C (cotton flannel) is representative of a successful durable flame-retardant garment treatment; all samples, plain, white, and blue, were flame retardant after either 50 W-TD or 50 W-LD cycles. However, this treatment might not be too satisfactory for curtains or other fabrics subjected to continuous exposure and then to laundering. After 2 weeks of exposure all samples failed after 25 launderings; after only 4 weeks all failed after 5 cycles.

Commercial Sample D (jean cloth) untreated passed 50 W-TD cycles but failed at 40 W-LD cycles. The blue and white samples both passed all 50 cycle tests. In contrast to Sample C above, Sample D showed a high degree continuous exposure resistance. The unpigmented samples passed 50, 25, and 25 wash cycles after 2, 4, and 6 weeks' exposure. The pigmented samples all withstood 50 wash cycles for the 2, 4, and 6 weeks' exposure.

THPOH-NH₃ treated fabric is apparently quite sensitive to sunlight. While the W-TD samples withstood 25 laundry cycles, the plain and white samples failed after 10 W-LD cycles and the blue after 15. This is also apparent in the continuous exposures. After 7 days the plain sample failed after only one washing and the white and blue after five washings.

APO-THPC is evidently a light-durable treatment. The W-LD tested samples passed at 40 cycles but failed at 50 cycles. All other samples of this set passed the standard verticle flame test after 50 wash cycles.

THPC-U-M shows essentially the same test results as the APO-THPC above, with the exception of the 6 weeks' exposure series. Here the durability of the plain and the blue samples drops to the 25 cycle test interval.

THPOH-U-M treated cotton shows the protection effect of the pigment finish. Plain fabric passed 20 W-LD cycles while the pigmented remained durable through 30 cycles. Similar results are shown in the continuous exposure-W-TD series.

The olive drab dyed sateens finished with THPOH-NH₃ or THPC-U-M performed in a manner very similar to their plain sateen counterparts. They are a little

more resistant to light damage than the unpigmented but, generally, not quite as resistant as the pigmented fabrics. This may be due, in part, to the fact that the dyed fabrics were treated with the flame retardants after dyeing; thus, a portion of the flame retardant is "on top" of the dye and unprotected from the sun. The pigments, on the other hand, were applied as the last step; hence, they would be better located to screen the flame-retardant polymer from degrading light rays.

CONCLUSIONS

In the commercial flame-retardant fabrics tested, the pigment after treatment, in three instances out of four, increased the number of times a sample could be washed and line-dried and still pass the vertical flame test. This increase in durability was evidenced by all of the pilot plant samples tested.

Wash and tumble dry cycles are not an adequate test for flame retardancy durability. While only two of 10 unpigmented samples failed to pass 50 W-TD cycles, only one of 10 passed 50 wash-line dry cycles.

As the work reported herein was conducted from February 25, 1970, to April 17, 1970, a final caution should be noted. The first third of the year, namely, January, February, March, and April, in total averages only about 20 percent of the annual solar energy. Had these tests been conducted during May, June, July, and August, when the solar energy averages about 62 percent of the annual total, the degradation of the line-dry (and other exposed) samples might have been as much as three times greater.

METHYLOL DERIVATIVE OF TRIS(2-CARBAMOYLETHYL)PHOSPHINE OXIDE AS A FLAME RETARDANT FOR COTTON [SUMMARY]

by

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(Presented by Cletus E. Morris)

Previous research at the Southern Regional Research Laboratory showed that a methylol derivative of tris(2-carbamoylethyl)phosphine oxide could be used to impart high wrinkle resistance and moderate flame resistance to cotton fabric. However, at the add-on levels studied (up to 14 percent) the treated fabric failed the standard vertical flame test. Recent commercial acceptance of higher flame-retardant add-ons prompted further study of this product's potential in flame-retardant finishing.

Tris(2-carbamoylethyl)phosphine oxide (TCPO) was prepared by adding potassium hydroxide to a mixture of acrylamide and white phosphorus. Yields of partly purified TCPO were 48 to 61 percent. TCPO was methylolated by treating it overnight at pH 10 with 3.2 moles of formaldehyde per mole of TCPO. The reaction product was not isolated, but was assumed to consist mainly of tris(N-methylol-2-carbamoylethyl)phosphine oxide (TMCPO), $OP(CH_2CH_2CONHCH_2OH)_3$.

Cotton sateen (8.2 oz./sq. yd.) was padded through 30 to 45 percent TMCPO solutions containing 1.5 percent softener and 0.5 to 2 percent of a mixture of citric acid and $MgCl_2 \cdot 6 H_2O$ in a 1:1 molar ratio. It was dried at 85° C. and cured for 3 to 5 minutes at 150 to 170°.

Treated fabric with an add-on of 21 percent or more, which corresponds to a phosphorus content of 1.9 percent or more, had a char length of 5 inches or less in the standard vertical flame test. When a 40-percent TMCPO solution was used, the required add-on was attained by using 1-percent mixed catalyst and curing for 5 minutes at 160° C. Fabrics treated under these conditions had a char length of less than 5 inches after 20 launderings, but failed the vertical flame test after 30 launderings. This treated fabric retained 78 percent of its original breaking strength, 65 percent of its tearing strength, and 83 percent of its flex abrasion resistance. The treatment imparted some stiffness to the fabric, but most of the added stiffness was removed by one laundering. The conditioned and wet wrinkle-recovery angles were about 265° (W+F).

Fabric treated under the conditions described above still passed the vertical flame test when one-fourth of the TMCPO was replaced by trimethylolmelamine, but it was much stiffer. Furthermore, the added stiffness was not so greatly reduced by a single laundering as was the case when TMCPO alone was used.

Aging a TMCPO solution containing the mixed catalyst overnight before applying it led to slightly increased efficiency, based on resin add-on, and to higher conditioned wrinkle recovery. However, stiffness also was increased.

The conditions under which TCPO was methylolated were varied to find out whether this would affect properties of the TMCPO-treated fabric. In one case the reaction time was shortened to 2 hours and in another case the reaction mixture was kept at room temperature as the exothermic reaction proceeded. In neither case was there an appreciable change in efficiency or in stiffness of the treated fabric. In both cases, as well as in the case of the usual methylation conditions, the atomic ratio of nitrogen to phosphorus in the treated fabric was 2.7 to 2.8:1 instead of the theoretical 3:1. Using only two moles of formaldehyde per mole of TCPO led to considerably lower efficiency.

In previous research at this laboratory, it was found that TMCPO-treated fabric was damaged in the chlorine retention test. However, the fabric does not yellow when bleached in hypochlorite.

The durability of the TMCPO finish to laundering was improved by increasing the TMCPO content of the treating solution from 40 percent to 45 percent or by increasing the curing temperature from 160° to 170° C. In both cases the treated fabric passed the vertical flame test after 40 or more launderings. The increase in curing temperature led to increased efficiency, but also led to increased stiffness and greatly decreased flex abrasion resistance; there was little change in breaking strength, tearing strength, or wrinkle resistance.

EFFECTS OF MOLE FRACTION OF "THPOH" IN THPC-"THPOH" FORMULATIONS AND CURE CONDITIONS ON FLAME-RETARDANT FABRICS [SUMMARY]

by

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Durable flame retardants based on tetrakis(hydroxymethyl) phosphonium chloride, (THPC), have met with moderate commercial success. More recently, THPC was converted to a compound hereinafter referred to as "THPOH" and this new product is the basis for additional flame retardants. The product was made by adding about 0.8 to 1.0 mole of sodium hydroxide per mole of THPC in solution.

Systematic studies to determine the relative value of THPC and THPOH in flame retardant processes have not been reported previously. This paper reports data showing the importance of the molar fraction of THPOH in THPC-THPOH flame-retardant formulations on the properties of fabric treated by various processes. Thus, comparisons were made of textile treating formulations in which the methylol phosphorus compounds were THPC, a mixture of THPOH and THPC, and THPOH. The molar fraction of THPOH in the treating formulations was varied by adding increments of sodium hydroxide to THPC. As increments of sodium hydroxide are added to THPC, the concentration of THPOH is increased at the expense of the THPC until essentially pure THPOH exists at a pH of about 8.8.

Cotton sateen fabrics were treated with flame retardant formulations in which the mole fractions of THPOH were 0.02, 0.11, 0.36, 0.75, 0.94, and 0.98. Three techniques evaluated for curing the formulations in cotton fabrics were heat cure, steam cure, and ammonia cure. When the heat or steam cures were used, the flame retardant formulations also contained urea and

trimethylolmelamine. When the ammonia cure was used, only THPOH and THPC were present. The total concentration of chemical agents in all formulations was held constant at 35 percent of the weight of the solution.

Changing the proportions of THPOH/THPC in flame retardant formulations had little effect on add-on of retardant, char length, and moisture regain of treated fabric but did have significant effects on most other fabric properties including breaking and tearing strengths, and durability of the finish. The method of curing had significant effects on wrinkle recovery and stiffness of treated fabrics. With respect to stiffness the steam curing technique used in this study produced excessive stiffness, otherwise fabric properties were good. The stiffness is caused by interfiber deposits of flame retardant. Heat curing avoided stiffness and imparted the generally desirable property, wrinkle recovery. The outstanding features of the ammonia cure were high tearing and breaking strengths without imparting stiffness. The one factor that had the greatest influence on durability of flame retardant regardless of curing technique was the proportion of THPOH to THPC used in the treating formulations. Although durability was generally acceptable regardless of mole fraction, the best durability was obtained from formulations in which the mole fraction of THPOH was about 0.94. Because some flame retardant is lost from all of the finishes during early stages of the alkaline boiling test, it is necessary to apply about 20 percent more flame retardant to a fabric than is needed to provide the desired degree of durable flame retardancy.

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